Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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DISCLAIMER

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October 2018

Savannah River National Laboratory ™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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ACKNOWLEDGMENTS

EXECUTIVE SUMMARY

This report documents the results of sealed reactor tests to measure the hydrogen generation rate (HGR) from Tank 50 waste, which may be on the order of 10^{-10} (ft^3/h)/gal. Because the estimated HGR limit of detection (LOD) for an open, continuous flow system is approximately 10^{-7} (ft^3/h)/gal a more sensitive method was needed. By accumulating generated gasses in a sealed system without a continuous purge gas, the resulting concentrations can increase the sensitivity of measurement, which is based on time of heating.

In 2017, Savannah River Remediation (SRR) declared a Potential Inadequacy in the Safety Analysis (PISA) in each of three Liquid Waste facilities: Concentration, Storage and Transfer Facility (CSTF), Saltstone Production Facility (SPF), and the Defense Waste Processing Facility (DWPF). The research for this report concerns waste from Tank 50 which feeds Saltstone. This study evaluated the impact of organics including formate on the generation of flammable.

The task included heating Tank 50 sample(s) of salt solution at varying temperatures (e.g., 50°C, 75°C, 100°C, and 120°C) to determine if organic compounds are decomposing into H_2. Testing also included a non-radioactive salt simulant of Tank 50 spiked with organics expected in Savannah River Site (SRS) tank waste. In addition, the tests included the addition of grout-premix and Blast Furnace Slag (BFS) to determine if any solid phase reactions are present, which would accelerate or inhibit the generation of H_2 at these temperatures.

The equipment shakedown tests demonstrated the designed sealed reactor could adequately and accurately measure HGR. These tests provide the following highlights.

- Pre-test pressure evaluation of the reactors found no leaks when using helium, which demonstrated that the reactors are impermeable to H_2, which is a less permeable gas.
- A known mass of H_2 introduced into the reactors was accurately measured after heating and sampling thus confirming the reactors to be leak tight.
- Tramp organic species in the sodium hydroxide produced H_2 which limited the lowest quantification achievable for any examined additives.
- Shakedown testing with caustic demonstrated a HGR lower limit of quantification (LOQ) ~ 4 x 10^{-9} (ft^3/h)/gal; therefore, longer-duration tests were planned for simulant and radioactive waste tests to pursue lower LOQs.

The second phase of testing used non-radioactive simulant of Tank 50 waste and various additives. The findings include the following.

- A test with simulated Tank 50 samples at 115°C ± 5°C (for 4.7 hours) under an air atmosphere showed a measurable increase in HGR compared to a test blanketed by nitrogen.
- At 24°C ± 3°C (for 7.6 days), the HGR was approximately 7 x 10^{-10} (ft^3/h)/gal, demonstrating the ability to achieve measurements at the targeted sensitivity.
- Tests at 93°C ± 7°C (for 5.2 hours) with formate added at prototypical concentrations showed no statistically discernible H_2 production above the background attributed to tramp organics in the caustic simulant.
- Tests at 94°C ± 4°C (for 4.4 hours) containing grout-premix and a lignin organic spike (Admix) produced markedly more H_2. Upon review of the data, and given that Admix is currently prohibited from use in SPF, testing with Admix was discontinued.
- Manufacturing of monosodium titanate (MST) may leave residual organics that could contribute to thermolytic generation of H_2 in Tank 50 and downstream processing. Tests exposing Tank 50 simulant at 94°C ± 6°C (for 4.9 hours) with filtrate from MST added showed no statistically discernible H_2

production above the background attributed to tramp organics in the caustic simulant. The HGR was approximately 2 x 10^{-7} (ft^3/h)/gal. Testing with MST filtrate was discontinued.

- Tests at 94°C ± 3°C (for 6.2 days) with 247 mg/L Total Organic Carbon (TOC) as Modular Caustic Side Solvent Extraction Unit (MCU) solvent in the Tank 50 simulant showed no statistically discernible H$_2$ production above the background attributed to tramp organics in the caustic. The HGR was approximately 3 x 10^{-8} (ft^3/h)/gal. Testing with MCU solvent was discontinued.
- Tests with either grout-premix or BFS added to the Tank 50 simulant indicated H$_2$ production more than that attributed to the tramp organics in the caustic simulant. Testing of these additives continued with radioactive waste samples.

The final phase of the tests examined radioactive Tank 50 samples with either grout-premix or BFS added.

- The difference in the rate of production of H$_2$ for an overlaying air or nitrogen atmosphere appears insignificant.
- Presence of BFS and grout-premix increases the HGR with a maximum measured rate of approximately 1.0 x 10^{-6} (ft^3/h)/gal at ~115°C. The difference between BFS and grout-premix was not significantly different within a 95% confidence level.
- Assuming a first order Arrhenius dependency, testing provides an average activation energy of 82.6 ± 9 kJ/mol for all the Tank 50 samples, as well as for Tank 50 samples with added grout-premix or BFS. However, when excluding room-temperature, 32°C, test results to consider the primarily effect of thermolysis, then the average activation energy is similar at 83.1 ± 12 kJ/mol, but containing slightly more uncertainty. This value is comparable to that derived for thermolysis of organic constituents in Hanford Site waste.
- The experimental HGR results are bounded by calculated values based on the Hu equation adjusted to 25°C, following the literature protocol and the characterization data for the Tank 50 samples.
- Testing of Tank 50 samples at 32°C (for 26 days) showed an average HGR of 1.32 x 10^{-9} (ft^3/h)/gal ± 0.14 x 10^{-9}. This result is the same order of magnitude to the Monte Carlo n-Particle Code estimate of radiolytic rate of 5.1 x 10^{-10} (ft^3/h)/gal from a 180-mL batch of waste. Furthermore, the result is conservatively bounded by the estimated SRR Waste Characterization System (WCS) radiolytic value for supernatant of 3.09 x 10^{-9} (ft^3/h)/gal and 5.08 x 10^{-9} (ft^3/h)/gal for slurry.
- Gas analyses from tests with Tank 50 (with and without added BFS or grout-premix) at 115°C showed ultra-trace quantities of an unidentified species. This temperature exceeds the operating limits for either Tank 50 or for SPF and the Saltstone Disposal Units (SDUs). Additional experimental work would be needed to identify the species.
- Longer testing periods give more accurate results, but the effect appears to reach an asymptote after 6 days.
- Simulant and radioactive results are in good agreement.

Additional testing is warranted to understand the contribution of BFS and grout-premix to thermolytic H$_2$ generation at conditions more applicable to SPF and the Saltstone Disposal Facility (SDF). These tests added limiting amounts of the solids to the Tank 50 samples. Interpreting the implications for SPF and SDF requires experiments that examine prototypical process concentrations and that examine the full curing cycle. A risk exists that higher concentrations of the additives will results in higher peak HGRs than indicated by the tests documented within this study.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption
AC&P	Advanced Characterization & Processing (Group)
ACS	American Chemical Society
BFS	Blast Furnace Slag
CPT	Chemical Processing Technologies (Section)
CSTF	Concentration, Storage and Transfer Facility
CVAA	Cold-Vapor Atomic Absorption
DAS	Data Acquisition System
DSA	Document Safety Analysis
DWPF	Defense Waste Processing Facility
ELN	(SRNL) Electronic Notebook [L0833-00239-05, -06, -07, -08]
ES	Environmental Stewardship (Directorate)
GC	Gas Chromatograph
HAS (eHAP)	The electronic Hazardous Analysis Process was revised to Hazardous Analysis System after the start of this project.
HGR	Hydrogen Generation Rate
HPLC	High Performance Liquid Chromatograph
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IT	Immobilization Technologies (Section)
LIP	Liquid Introduction Port (on the sealed reactors)
LOD	Limit of Detection
MCU	Modular Caustic Side Solvent Extraction Unit
MRL	Method Reporting Limit
MST	Monosodium Titanate
PISA	Potential Inadequacy in the Safety Analysis
ppm	Parts Per Million
PTP	Process Technology Programs (Group)
%RSD	Percent Relative Standard Deviation
SDF	Saltstone Disposal Facility
SDU	Saltstone Disposal Unit
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation

SRS   Savannah River Site

SVOA   Semi-Volatile Organic Analysis

TIC   Total Inorganic Carbon

TOC   Total Organic Carbon

VOA   Volatile Organic Analysis

WAC   Waste Acceptance Criteria

WCS   Waste Characterization System

WPT   Wasteform Processing Technologies (Section)

1.0 Introduction

In February 2017, Savannah River Remediation (SRR) declared a Potential Inadequacy in the Safety Analysis (PISA) in each of three Liquid Waste facilities: Concentration, Transfer and Storage Facility (CSTF), [7.1] Saltstone Processing Facility (SPF), [7.2], and the Defense Waste Processing Facility (DWPF) [7.3]. The PISAs relate to how organics can impact the radiolytic and thermolytic production of H_2, which is a flammable gas. Parallel studies are evaluating the impact of organics on the generation of flammable gases in the vapor space within Savannah River Site (SRS) High-Level Waste (HLW) waste tanks and evaporator systems [7.4, 7.5, 7.6, 7.7, 7.8, 7.9]. The impact of organics on radiolysis in DWPF is currently addressed using a combination of previous testing and revised calculation methods [7.10, 7.11]. This report focuses on testing for Tank 50 and related downstream processing for Saltstone Disposal Facility (SDF).

As requested in a Technical Task Request (TTR) issued by SRR, Savannah River National Laboratory (SRNL) performed thermolysis testing to close gaps associated with the PISAs [7.12]. The overall technical plan is detailed in the Task Technical and Quality Assurance Plan [7.13].

Radioactive samples were used for some of the testing, allowing for a measurement of thermolytic Hydrogen Generation Rate (HGR) with the mixture of organics present in the radioactive waste. A separate report [7.14] determined the amount of radiation energy retained within the liquid. Using this information, the Run Plan (described later in Section 3.0) allows separate determinations of the radiolytic and thermolytic contributions to H_2 generation.

Studies for Hanford Site waste tanks indicate chemical decomposition by radiolysis and/or thermolysis as important mechanisms for the generation of H_2 in the Hanford Site HLW system. There are significant differences in the composition of waste between the Hanford Site and SRS. Because of those differences and no prior evaluation of thermolysis occurring within the SRS waste tanks, the testing described below is intended to determine the thermolytic contribution to flammable gases in the Tank 50 matrix.

This report addresses Task 6 of the TTQAP [7.13]. That task involves testing a sample from Tank 50 at varying temperatures (e.g., 50°C, 75°C, 100°C, and 120°C) to determine if organic compounds are decomposing into H_2. Testing also included a non-radioactive salt simulant of Tank 50 spiked with organics known to be present in either Tank 50 or downstream process operations. In addition, the testing included the addition of Blast Furnace Slag (BFS) to determine if any solid phase reactions are present which would accelerate or inhibit the generation of H_2 at those temperatures of interest.

The TTR requested that the H_2 LOD be as low as reasonably achievable to allow measurement of the predicted low HGR [7.12]. For example, temperatures or purge rates could be adjusted to allow a lower LOD. A Sealed Reactor System was designed because the HGR LOD for an open, continuous flow system is approximately 1 x 10^{-7} (ft³/h)/gal. Quantification of HGR below this limit, like the estimated rate of 3 x 10^{-9} (ft³/h)/gal for Tank 50 waste, requires an alternate measurement system. By accumulating generated gasses in a sealed, closed, system and avoiding use of a continuous purge gas, the H_2 concentration increases thus improving the sensitivity of measurement. Design of a sealed system implies obtaining no or very low permeability and was based in part on successful past designs [7.15, 7.16, 7.17]. The selection of sealing surfaces and material is important to minimize the loss of generated gasses. The sealed system allows placing a measured sample mass inside a robust vessel of known volume. Testing held the apparatus at temperature for a measured duration and stirred continuously using a stirrer/hotplate. At the end of a selected period, the headspace of the reactors was sampled, utilizing a gas chromatograph (GC) to measure the H_2. From the concentration of H_2 and elapsed time, one determines the average thermolytic HGR for the sample over the test period. Tests were performed at multiple temperatures to calculate an activation

energy of the thermolytic HGR assuming a first-order Arrhenius equation. All applicable piping and the pressure vessel was designed to meet ASME code B31.3 [7.18].

2.0 Experimental Equipment

Besides the test solutions and gases, the principal part of the experimental setup was the sealed reactor to contain the evolution of H_2 from a test solution. The supporting equipment included heating and stirring plates, measurement and data acquisition system (DAS), gas and liquid sampling equipment, safety equipment, e.g., overtemperature control.

2.1 Sealed Reactors

Eight reactors were constructed of 304 stainless steel, which is impermeable to H_2 below 150°C [7.19]; more so than 316 SS [7.20, 7.21]. (Per procedural requirements, one reactor was subjected to burst testing to establish the maximum allowable operating pressure.) The remaining seven reactors, equipped with purging and sample valves, but without the pressure transducers, were leaked check with helium to 150 psig. They were shown to have a leak rate of less than 10^{-9} cc/sec He, which implies a lower rate for H_2 due to being a larger molecule. Figure 1 shows a schematic of the finished reactor with two control valves installed, a pressure transducer, and the liquid introduction and sampling port sealed.

2.1.1 Reactor Preparation and Volume Calibration

The reactors were built for sealed operation and the first steps needed before testing was to prepare the vessels so that the vessels themselves would not lead significant uncertainty in the H_2 results. They were cleaned, passivated in 20 vol% nitric acid (4.8 M), and baked at 600°F for > 4 hours under vacuum to remove residual H_2 from the steel. On completion of reactor preparations all the reactors were checked to confirm they met ASME B31.3 code specifications for Pressure Protection; one reactor was sacrificed in a burst test. It held leak tight until 2800 psig when the large conflat seal began to slowly leak.
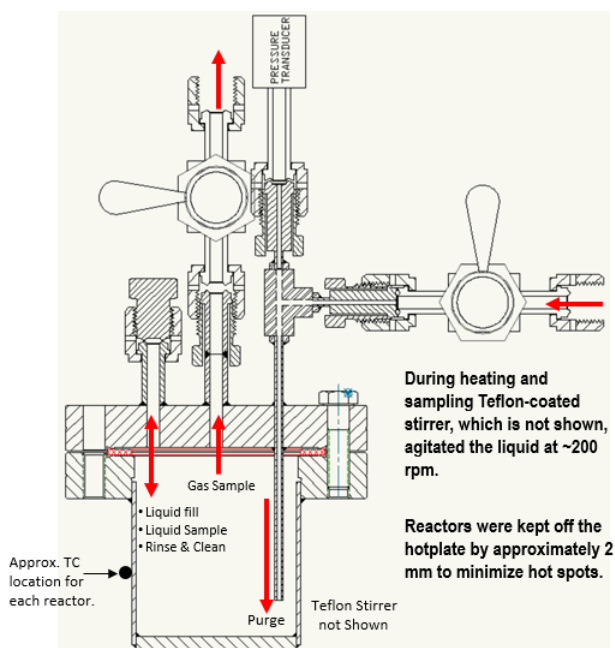
Figure 1. Sealed reactor

Figure 2 shows a reactor during several stages of its preparation, including after machining and welding. Figure 2(a) show the reactor before being cleaning (to remove organics), after passivating in nitric acid (to build an oxide coat to minimize permeability), then baking in an inert atmosphere (to remove any H_2 within the steel), and pressure testing (to determine sealability). Figure 2(b) shows one vessel fully assembled and ready for a pressure test.

(a) (b)

Figure 2. (a) shows the top and bottom inside of a reactor and the conflat seal, (b) shows the closed reactor ready for testing.

After the preparation, each reactor was calibrated for its internal volume with water, so the liquid added and gas head space could be accurately known for testing. The volumes are found in Appendix A, Table 12. The reactors were design to have 200 mL of internal volume they were closer to 195 mL when calibrated. Note, a Teflon-coated magnetic stirrer was added to each before being sealed. The volume of each 3/8-inch diameter by 1.5-inch long stirrer is 2.715 mL. This volume is not included in Table 12; however, each head space volume is reduced by the stirrer volume when calculating the HGR.

2.1.2 Reactor Pressure Evaluations

To meet the American Society of Mechanical Engineers (ASME) standard B31.3, ASME Code for Pressure Piping, as implemented by WSRC-IM-95-58, Engineering Guide 15060-G, Application of ASME B31.3, the vessels were exposed to both theoretical and mechanical evaluations. The theoretical evaluation is documented in site Calculation M-CLC-A-00605, Rev. 0, Conflat Hydrogen Generation Vessel [7.22]. The theoretical evaluation concluded that the vessels as designed are qualified for continuous service up to 150 psig, and 300°F concurrently.

After the theoretical evaluation, a sample vessel, HGV-1, was removed for proof testing, taking the vessel to hydraulic failure, using water pressure. This testing is documented in the calculation, and the burst pressure achieved was 2,837 psig. After the B31.3 required devaluation for ductile materials, the final proof pressure was 938 psig. The vessel is limited to the theoretical values of 150 psig (1034 kPa$_g$), and 300°F (149°C), concurrently.

2.2 <u>Overall Sealed Reactor System</u>

The basic arrangement for all tests was the same. Figure 3 depicts the reactors in the process of being filled. Reactors HGV-2 to HGV-5 are on the large stirrer/hotplate to the left; HGV-7 and HGV-8 are on individual stirrer/hotplates to the right. With HGV-6 missing it is possible to see the reactor well in the aluminum block and the thermocouple placement in the well. The aluminum block served the following functions.

1. More uniformly distributed the heat from the stirrer/hotplate so all the involved reactors would remain close to each other in temperature.
2. Positioned the reactors to align with the magnetic stirring location.
3. Anchored the thermocouples (TCs) in the thermal well so the TCs were located at approximately the center point of a reactor body, see Figure 1.
4. Supported the reactors so they sat about 2 mm off the stirrer/hotplate center to minimize hotspots.
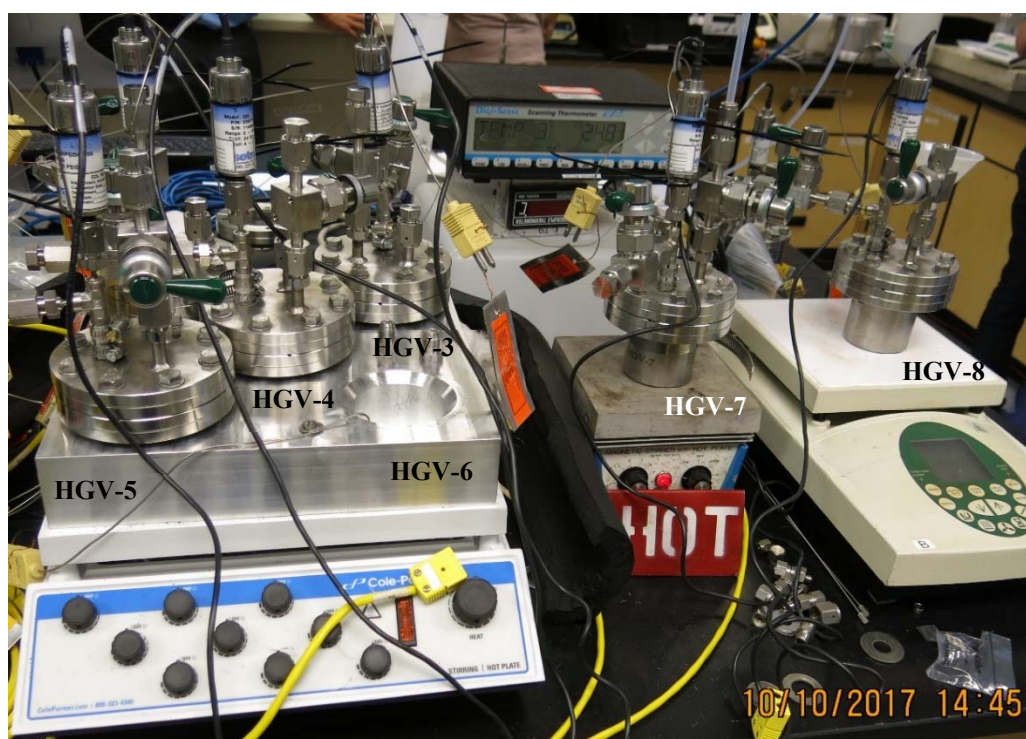
Figure 3. Sealed reactors on stirrer/hotplates.

To fill a reactor, it is removed from its stirrer/hotplate, then the liquid port is slowly opened, Figure 4(a). Any residual pressure from the previous test is monitored to avoid an energetic release of gas or liquid. A funnel is inserted, Figure 4(b), after a custom-made fitting is installed to secure the funnel and prevent leaks.

(a)   (b)
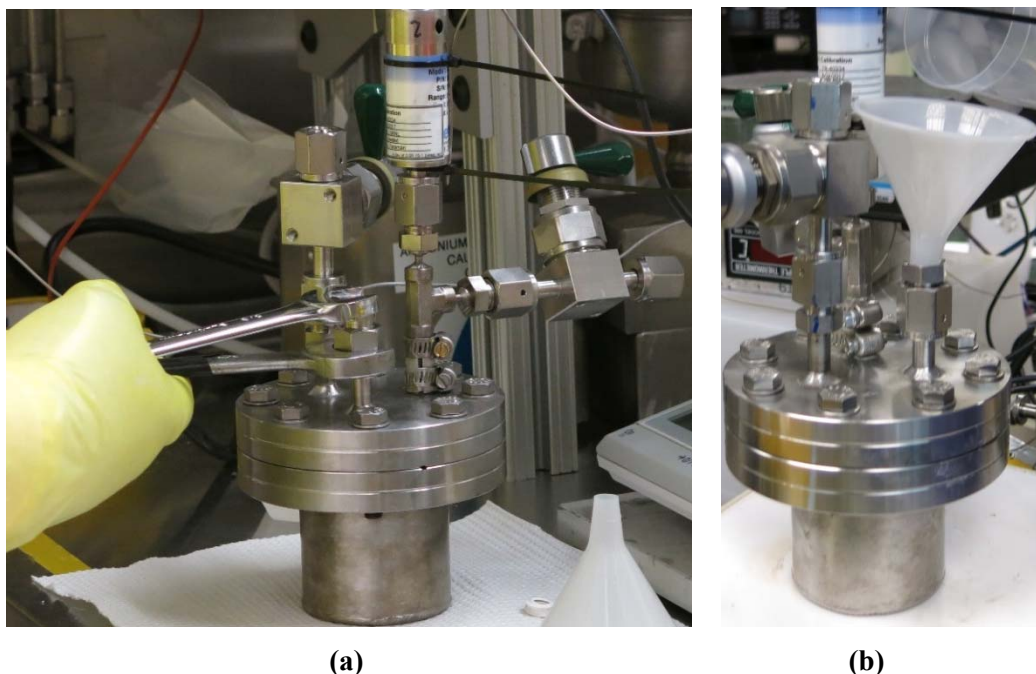
Figure 4. (a) Shows opening the VCR-sealed liquid port and (b) shows filling the reactor.

Generally, the 5 reactors on the large stirrer/hotplate were used over the entire range of temperatures and the reactors on the two-individual stirrer/hotplates, i.e., HGV-7 and HGV-8, were typically used for lower-temperature tests. However, these two separate reactors were also used for some of the higher temperature tests and when so, the reactors were raised approximately 1 to 2 mm off the surface of the stirrer/hotplate with metal washers. Those two reactors secured their TCs on the outside of the reactor wall with pipe clamps, as shown in Figure 5, before it was insulated.

Figure 5. Single reactor on hotplate with TC placements before insulation.

Once the reactors were filled with test solution and purged with a test gas, they were fully connected to the DAS and insulated to minimize heat loss, as shown in Figure 6. The test setup shown in this figure was used during shakedown and simulant operation. For radioactive service, this equipment was moved to a radioactive hood. However, the setup was similar, as in Figure 7 which shows the sealed reactors enclosed with insulation. The GC is visible to the left.
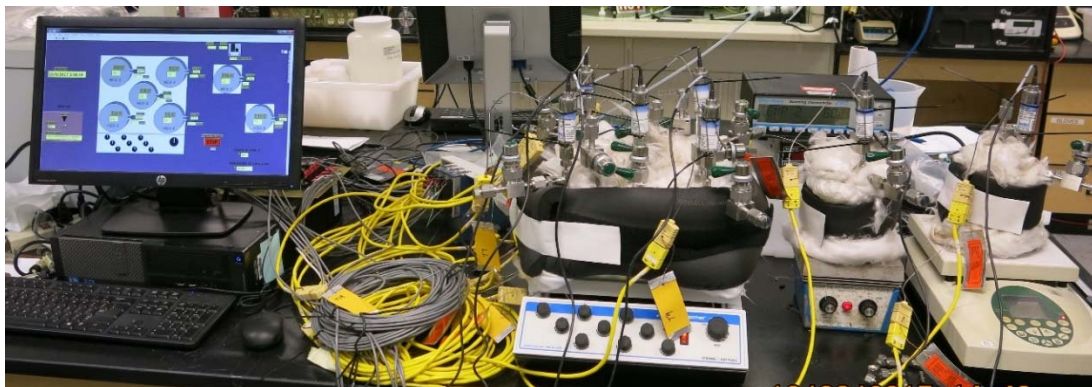
Figure 6. The overall sealed reactor setup for shakedown and simulant tests. The sealed reactors are covered with insulation and the DAS is to the left.

Figure 7. The overall sealed reactor setup for radioactive tests with the GC to the left.

To collect a gas sample during shakedown and non-radioactive testing, after the reactors reached room temperature each reactor was removed from its stirrer/hotplate and placed on another stirrer to continue mixing the contents while sampling was performed. For radioactive tests, the reactors were in a vent hood, so they were left in place to mix and sample.

2.3 <u>Test Operation with Simulant and Radioactive Waste Testing</u>

The operation for both simulant and radioactive tests were very similar, with the differences being due more to the different locations and the added precautions necessary when working in a radioactive environment. The basic method of testing is as follows.

- Have cleaned and ready the number of reactors for each test as well as all the supporting equipment, including the DAS, tools, seal, liquid, test solutions, spike materials, etc. Note that a Teflon-coated stir bar was already introduced into each reactor when they were sealed.
- Fill clean reactors with test solution and spike material. For volumes and spike additions see Appendix A for simulant and radioactive tests.
- Purge head space in each reactor with the appropriate gas of at least 15 times the internal volume of the space, then pressurize to 20 psig, and seal. This pressure was chosen because it was the highest acceptable by the GC and it provided sufficient gas in the smallest head space used of ~20 ml to be able to draw 5 or more gas samples. The purge is introduced under the liquid in the reactor, which agitates liquid; therefore, the purge rate is low (~200 cc/min) to not cause splashing.
- Place reactors on the stirrer/hotplates, insulate, energize both the stirrers and heat to reach the target temperature. Stirring is done gently, e.g., 200 rpm, to minimize splashing. When the target temperature was attained and steady to within ±5°C, the clock was started.
- After the target temperature was held for the target heating period, the stirrer/hotplates are de-energized, and the reactors allowed to cool overnight, or until the internal pressure was within 5 psi of the starting pressure, before measurement.
- Measure H_2, (typically, 5 to 7 replicates for each vessel).
- Pull a liquid sample from each reactor.
- Thoroughly drain, rinse, and dry all the reactors for the next test.
- Filter liquid samples if solids were present before submission for analyses.

2.4 <u>Measurement Equipment</u>

Appendix B contains a spreadsheet listing all the measurement and test equipment and Appendix C contains the measurement uncertainties determined from calibrations. The flowing sections describes some important aspects of the equipment.

2.4.1 Temperature

Each of the 7 reactors had two thermocouples (TCs) for a total of 14 TCs being monitored simultaneously when all reactors were employed. For each reactor, one TC was attached to the pressure transducer to monitor its temperature because the transducer had to be maintained below 75°C, and the second TC was attached to the outside body of the reactor to measure the reaction temperatures. (The pressure transducer temperatures are not reported.) The TCs on the reactor body were attached, or maintained close, to the reactor by being installed between the reactor and the reactor well in the aluminum block on the large stirrer/hotplate or held to the reactors with a pipe clamp for those vessels that sat on the smaller individual stirrer/hotplates. The TCs were not installed internally into the reactor to minimize penetrations that could increase the possibility of leaks. Hence, the internal and external temperatures differed.

Initially, since the pressure was measured internally it was thought that it could be used to obtain an accurate internal temperature based on the known starting temperature and pressure; however, water vapor was the largest contributor to the increased head-space pressure on heating. This complication prevented the use of pressure to be a reliable measurement for temperature. For example, Figure 8 shows the pressure increase

during heating for a sealed reactor half full of water that is being mixed. As is shown, the pressure is significantly above what would be expected using just the ideal gas law. In fact, the actual pressure closely follows the Antoine equation [7.23] that models the increase of water vapor pressure with temperature, starting with a reactor containing air at an initial pressure of 20 psig.
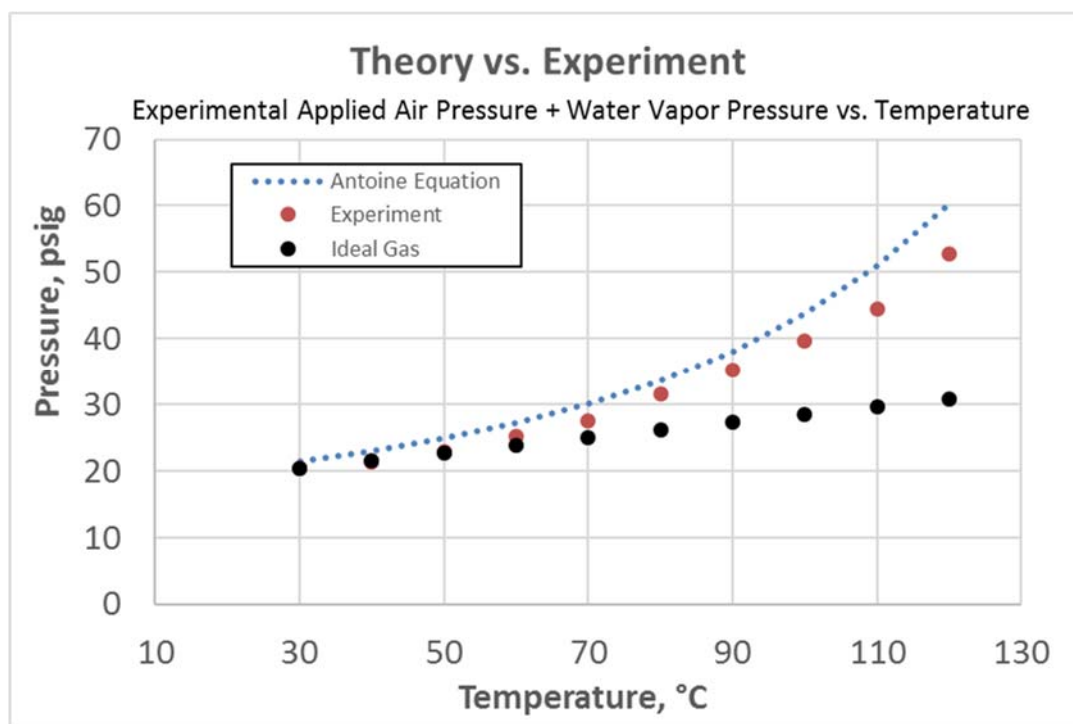
Figure 8. Typical pressure increased with temperature for sealed reactors.

To obtain a more accurate measure of the internal reactor temperatures a test was conducted after the completion of overall radioactive tests to measure the internal and external temperatures for the target temperature points used in testing. That is, from 20°C to 120°C. A reactor, HGV-4, which was the middle of the large stirrer/hotplate used during testing, see Figure 3, was set up with a calibrated TC that was located inside the reactor and submerged into the water pool, Figure 9. That reactor was filled with enough deionized water to leave a 100-mL head space (which was reduced to about 97 mL because of the volume of the stir bar) and the space was purged with air and pressured. Then the reactor was heated and held constant at multiple temperatures. The data are shown on Figure 10 and from those results steady-state points were obtained at each hold point.
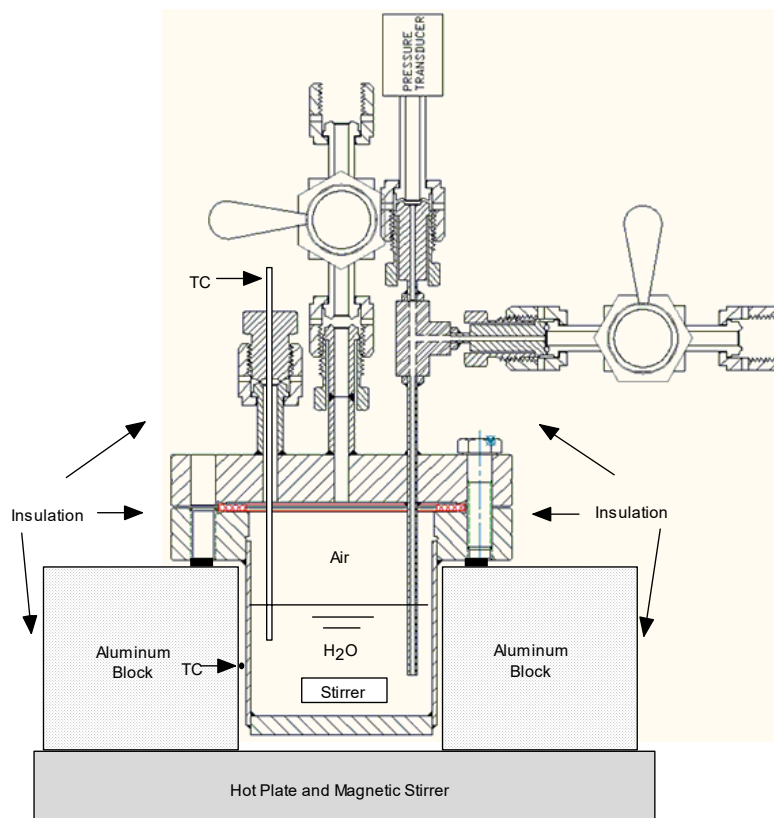
Figure 9. Temperature calibration assembly
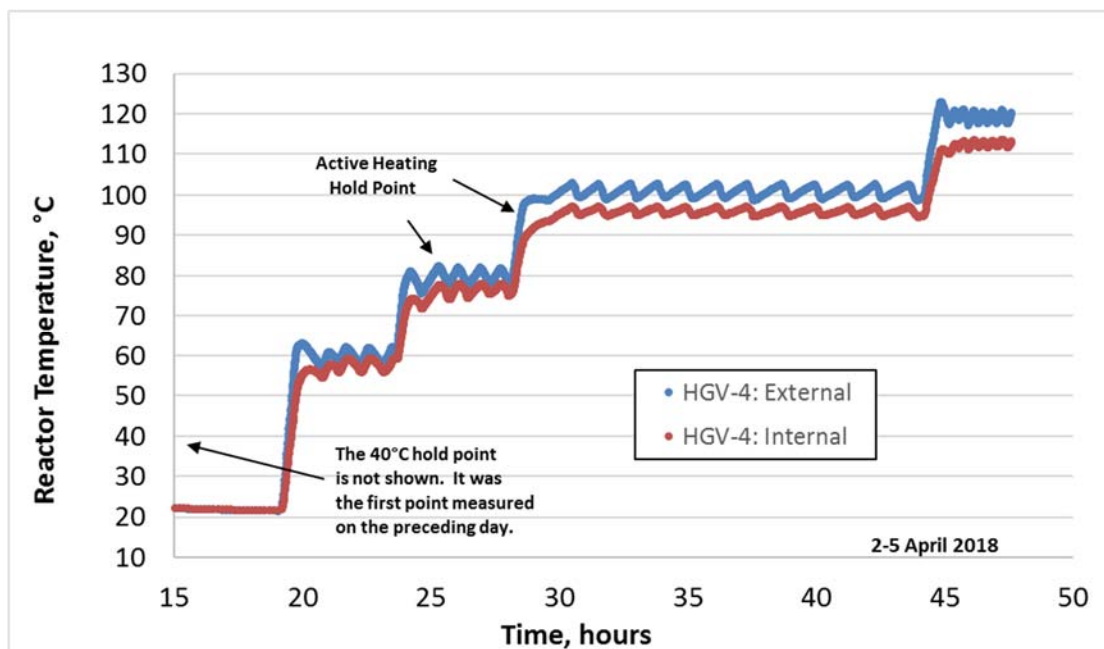
Figure 10. Sealed Reactor Internal vs. External Temperature starting at zero-gauge pressure.

The resulting temperature differences are shown in Figure 11 along with a best-fit curve displayed.
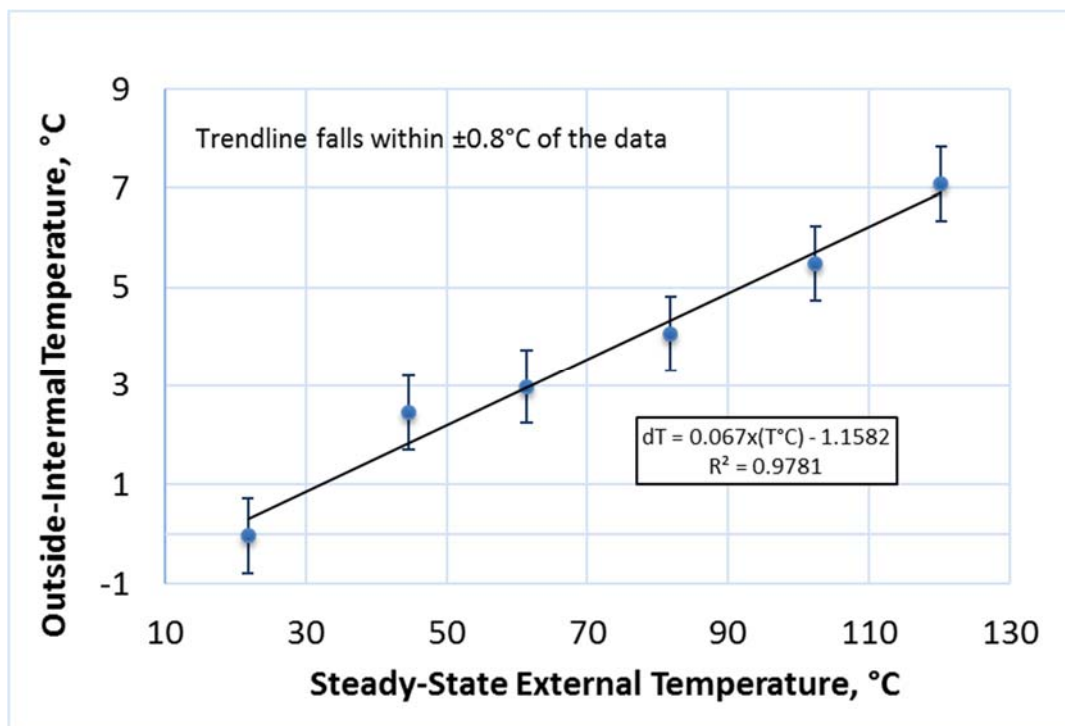
Figure 11. Correction to Measured Outer Temperature on Sealed Reactors

This information was used to adjust all the measured external temperatures. The equation used is:

$$\text{T, internal} = \text{T, external} - [0.067 \times \text{T, external (°C)} - 1.16°C] \qquad (1)$$

The temperature data from the simulant and radioactive tests were adjusted with this Equation (1).

It is important to note that this temperature correction was only done with one of the reactors located in one of the locations on the large stirrer/hotplate, see Figure 3 and Figure 7. As already mentioned, the middle location was chosen to be representative, however, the other locations will have a slightly different temperature environment. The correction was also used for the two reactors on the separate stirrer/hotplates where the thermocouples were clamped to the side of each reactor, approximately in the same location used to place the thermocouples next to the reactor bodies in the aluminum block. However, in most cases those separate stirrer/hotplates where used for the longer term low temperature tests, i.e., < 33°C for which the correction is < 1.1°C. This correction method is assumed to accurate to within the uncertainty of the thermocouples themselves of ~ ± 2°C

2.4.2 Pressure

To maintain the leak integrity of the vessel, a specific VCR® compatible pressure transducer was chosen to measure 0-150 psig pressure. The chosen model was the Setra® 225G-150P-G-D4-11-06. It had all 316L SS wetted parts, with an output of 4-20 mADC. It provided a less than 1×10^{-9} atm. cc/sec leak rate. The stated accuracy was ±0.25% Full Scale, with a temperature compensated range of 15 to 150°F (-9 to 66°C).

2.4.3 Gas Flow

Two flow measuring devices were used during testing, both clean and radioactive. For simulant testing, which was performed at the Aiken County Technology Laboratory, the transducer, M&TE FM1K-11, was used to meter air and nitrogen into the test vessels. FM1K-11, along with its readout, measured standard cubic centimeters per minute (sccm) of gas. It has a stated accuracy of ±2% of reading, and a range of 0-1000 sccm. It is made by MKS and is one of many MKS flowmeters used in SRNL. It internally compensates for both pressure and temperature, giving a standard mass flow value of gas flow.

For radioactive testing, a rotameter was used for similar service as the mass flow meter. The M&TE number for this rotameter is TR-40351, with a range of 51.8 to 517.8 sccm of air. Its stated accuracy was ± 25 sccm. Because it is a rotameter, the value indicated on the scale must be corrected for pressure and temperature in the metering tube. Since it was calibrated at atmospheric conditions, and its use in the lab required positive pressure in the tubing, i.e., pressure losses downstream of rotameter always caused greater than atmospheric pressure in the metering tube, then the indicated mass flow rate value was always conservative. That is, the value indicated was always less than the actual mass flow rate. This was deemed acceptable, as the rotameter was used to meet the minimum number of volume changes in the head space required by the procedure. Volume changes were determined by flow rate multiplied by the time interval, indicating volume of gas displaced in head space as a multiple of head space volumes.

2.4.4 GC - H_2 Measurement

In the sealed system testing, the reactor vapor space was filled with either nitrogen or a 20% oxygen, 0.5% krypton, balance nitrogen gas. Nitrogen was initially used for some testing in cases where high H_2 generation was postulated. The remaining tests used a H_2-free mixture of oxygen/krypton/nitrogen with no detectible helium, which can interfere with low level H_2 quantification. Both helium and H_2 in air can be detected with the micro GC.

Each reactor vapor space was sampled and characterized using an Agilent series 3000 micro GC. The GC has an on-board sample pump that can draw gas samples with pressures as low as atmospheric. For the sealed reactor tests the vapor/head space was filled with gas up to 20 psig to allow for multiple gas samples per reactor per test. The GC was configured with a Molsieve 5A column (Column-A) and a PoraPlotQ column (Column-B). In general, Column-A can be used to collect data related to helium, H_2, oxygen, nitrogen, krypton, and methane, while Column-B can be used to collect data related to carbon dioxide and nitrous oxide. However, the instrument was optimized to quantify low quantities of H_2, as this was the primary flammable gas of interest. Because sample gas was limited and interest in carbon dioxide and nitrous oxide was secondary, Column-B was not used.

When little or no H_2 generation was expected the GC was calibrated with a nominal 10pro ppm H_2, 20% oxygen, balance nitrogen gas standard. Due to the high sensitivity settings to quantify H_2, concurrent quantification of oxygen and nitrogen was not possible. From the calibrations, the limit of detection (LOD) for H_2 was determined to be 1 ppm, but the limit of quantification (LOQ) was 3 ppm.

2.4.5 Data Acquisition System.

A software package, Labview™, was used for the signal processing. A virtual instrument (VI) was programmed, with the front panel shown below in Figure 12, which shows an example of the test in operation as the stirrer/hotplates reached a target temperature of 120°C during shakedown testing. The VI received all the transducer signals, appropriately scaled them to engineered units, and displayed them. They were also recorded to a tab-delimited file when requested. Prior to completion of the assembly, the DAS

was calibrated per SRNL procedures (see Appendix C). Additionally, all instruments were calibrated per SRNL procedures. The following is a description of the signal processing hardware used.

Computer
Dell™ Optiplex 390 running Windows™ XP

Signal Processing Hardware
National Instruments™ Hardware
cDAQ-9174, signal processing chassis for C-Series Signal Modules
NI-9213, C-Series Temperature Input Module
NI-9205 (2), C-Series Voltage Input Module
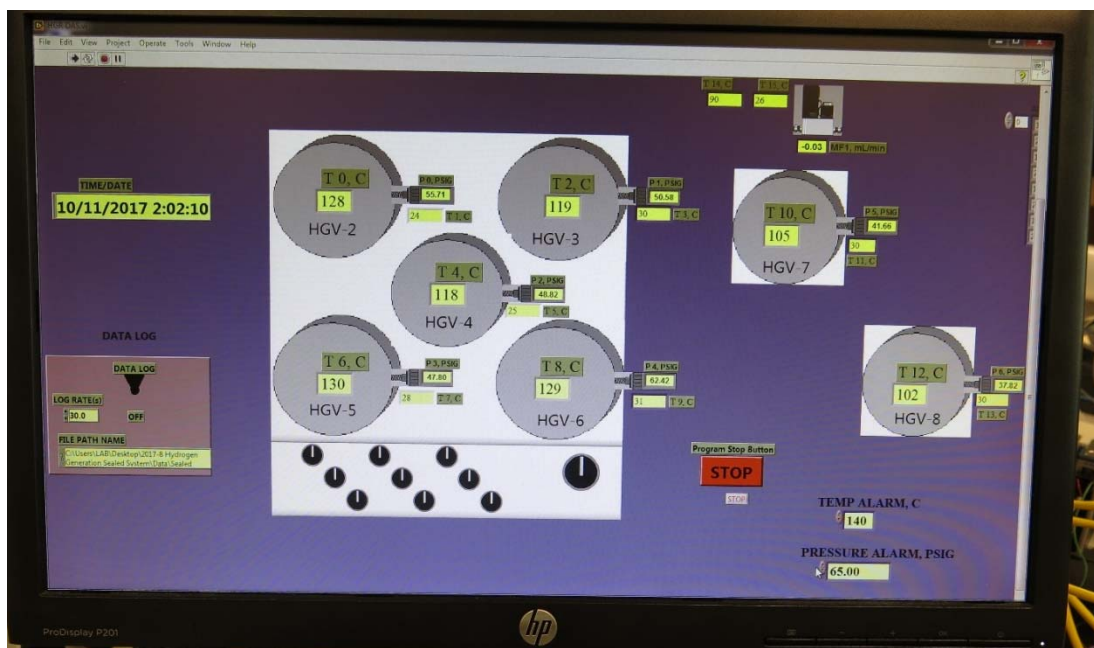
Figure 12. Photograph of DAS screen showing reactors HGV-2, 3, 4, 5, and 6 on main stirrer/hotplate, and reactors HGV-7, and 8 on individual stirrer/hotplates during a shakedown test.

3.0 Run plan

As per the run plan [7.24], the tests were divided into three campaigns: (1) shakedown tests to demonstrate the ability to accurately measure H_2; (2) simulant tests to help plan for radioactive tests; and (3) radioactive tests with Tank 50 samples to demonstrate the HGRs under conditions indicated in the TTR [7.12] and the TTQAP [7.13].

3.1 Shakedown Tests

To test the overall operation of the equipment and evaluate the ability to obtain accurate H_2 results several shakedown tests were performed. These tests examined: the adequacy of sealing, permeability to H_2, and the gas sampling method. In addition, these tests provided insight into the achievable H_2 detection level

for subsequent tests. Table 1 shows the tests from the Run plan. The first test added H_2-free air and examined for leak tightness at the highest planned operating temperature. The second test added a 10-ppm H_2 standard to examine the ability to sample with the GC and determine H_2 content at low concentrations. The remaining four tests evaluated overall reactor operation under test conditions of a small and large head space and the ability to measure a known amount of H_2 generated by aluminum dissolution. That is, these tests were to demonstrate that the overall experimental design was sufficient to accurately measure H_2 in sealed reactors. The liquid used to dissolve the aluminum was 1 M NaOH. First a test was performed without the aluminum to develop a baseline of any possible H_2 production from caustic itself because prior studies indicated tramp organics in the NaOH source material and corrosion could yield minor amounts of H_2 [7.25].

Table 1. Shakedown tests (4-hour duration at temperature)

Test No.	Test Type	Nominal (1) Temperature, °C	Start Pressure, psig	Fill Gas	Liquid	Amount of liquid, mL
1	Leak Tests	120	10 to 25	Air, No H_2	None	Zero
2	Standard H2	25	10 to 25	10 ppm H_2	None	Zero
3	1 M NaOH (2)	50	10 to 25	N_2, No H_2	1 M NaOH	180
4	Al pellet – 150 µg	50	10 to 25	N_2, No H_2	1 M NaOH	180
5	1 M NaOH (2)	120	10 to 25	N_2, No H_2	1 M NaOH	100
6	Al pellet – 750 µg	120	10 to 25	N_2, No H_2	1 M NaOH	100

(1) Nominal means ± 5°C
(2) Tests 3 and 5 lead-in tests, without the H_2 aluminum spike added to the 1 M NaOH, to determine a H_2 baseline from thermolysis of tramp organics and corrosion to obtain a more accurate measure for subsequent tests with Al pellets. The time at temperature was 4 hours followed by a night of cool down before measurements.

For Tests 4 and 6 the aluminum pellets were accurately weighed [see 7.27 in Experiment L0833-00239-05, "Mass of AL particles"] with a 5-place balance due to the very small size necessary to produce a known, but limited, amount of H_2. The masses of those pellets are shown in Table 2. While the nominal targets were 150 µg, for Test 4, and 750 µg, for Test 6, obtaining those exact quantities was not easy. However, knowledge of the exact mass used was more important than having the exact target size. Each mass dissolved was expected to produce a proportional amount of H_2.

Test 4 and 6 were performed by adding the small quantities of aluminum, listed in Table 2 to 1 M NaOH. The head space was purged, then filled with reagent grade H_2-free nitrogen, so the accumulated H_2 could be accurately measured after being produced from the following reaction:

$$2Al(s) + 2NaOH(aq) + 6H_2O \rightarrow 2Na^+ (aq) + 2[Al(OH)4]^- + 3H_2(g)$$
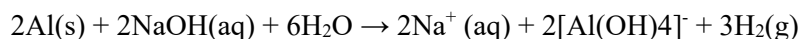
Pretrial tests showed the aluminum dissolved in 2 hours at 50°C and much faster at 120°C. Two tests were performed for 4+ hours at 50°C with a head space of 20 mL and 120°C with a head space of 100 mL; therefore, total dissolution was expected.

The sequence of the tests was the following.
1. Purge the head space with more than 15 head-space volumes using N_2.
2. Monitor the temperature and pressure with the DAS.
3. Heat reactors containing only caustic, i.e., without aluminum, for 4 hours.
4. Allow the reactors to cool and measure H_2 on following day with a GC.
5. Repeat Steps 1-4 after inserting a known mass of aluminum.

Note that the purge flow rates were low to prevent splashing of liquid due to the below-liquid purge tube. Purge rates varied between 200 and 300 mL/min. Also, the heating and sampling were accompanied with a gently stirring the liquid with a stir bar rotating at approximately 200 rpm.

Table 2. Aluminum pellets for shakedown tests

Test # >	4		6	
Reactor #	Al Mass µg	2σ µg	Al Mass µg	2σ µg
HGV-2	194.2	0.3	773.9	0.3
HGV-3	194.1	0.7	666.4	0.4
HGV-4	197.6	0.3	784.4	0.5
HGV-5	86.0	0.7	710.8	0.4
HGV-6*	274.1	0.3	na	na
HGV-7	201.6	0.5	663.2	0.2
HGV-8	613.1	0.3	705.5	0.4
Avg. Head	20 mL		100 mL	
Avg. Liquid	175 mL		95 mL	

Note that during Test 6 for HGV-6 the AL pellets was accidentally left out of the reactor. Distinguishing this small particle from a speck of dirt was challenging.

3.2 Simulant Tests and Radioactive Tests

Table 3 shows the average concentrations of key waste components from the four quarterly samples of 2016 plus the first two quarterly samples of 2017 (total of six samples, with each sample having its own data set).

3.2.1 Simulant of Tank 50 Waste

Simulant testing used a newly-formulated Tank 50 simulant based on quarterly sample data for Tank 50; for example, Crawford [7.26] issued such data for several quarters including 1Q 2017. An example of the direction used to make simulant can be found in Appendix D. The direction was used on several occasions when more simulant was needed. The actual directions for each batch can be found in the Electronic Laboratory Notebook (ELN) [7.27]. Table 3 shows the nominal concentrations of the simulant based on the six quarters (1st quarter of 2016 to 2nd quarter of 2017). The quarterly analyses have extensive tabulations of analytes, but only the major are chemicals shown in the table. The table provides the target concentration, as well as the measured concentration after preparation. No organic chemicals were intentionally added to the base simulant. Potassium was omitted because of its low concentration in the tank (~0.01 M), along with no expected potassium effect on H_2 chemistry.

Uncertainties in Table 3 are stated as % relative standard deviation (%RSD) of the data from the six quarterly reports. Note that the total sodium shown in the table was not obtained from the reports; instead, it is calculated as the concentration that balances the ionic charge of the individual species. However, the sodium %RSD was taken from the six sodium concentrations in the quarterly reports.

Simulant density was measured from the several batches made [see the ELN 7.27 in experiment L0833-00239-.5] and it was approximately 1.23 g/mL at room temperature to match the real waste or 1.237 g/mL (Appendix E, Table 20). The recipe in Table 3 contains only inorganic species but does not contain added silicon. Currently, the program has not yet determined whether silicon as silicate may play a direct role in HGR chemistry. A mechanism may form H_2 during formation of aluminosilicates and exchange reactions within the solution. It is known that formation of aluminosilicates will reduce the soluble aluminum. Because aluminum has been implicated as contributing directly to HGR; therefore, testing did not include any direct additions of silicon.

Table 3. Tank 50 waste & simulant for sealed reactor tests

Component Name	Mol. Wt. g/mol	Actual (1) M	Target (2) M	Simulant (3) M
Total Sodium	22.99	4.96	5.20 ± 7% (4)	4.96
Aluminate	95.00	0.15	0.15 ± 21%	0.15
Free Hydroxide	17.01	1.95	1.95 ± 11%	1.82
Nitrate	62.00	1.84	1.84 ± 4.2%	1.89
Nitrite	46.01	0.62	0.62 ± 10%	0.66
Carbonate	60.01	0.27	0.27 ± 57%	0.28
Sulfate	96.06	0.052	0.052 ± 9%	0.048
1. Average concentrations from samples taken over six quarters.				
2. Uncertainties are %RSD from six quarters of data.				
3. Analytical measurements of simulant used were ±10%.				
4. Na target value was determined by anion-cation balance of				
listed waste components, allowing sodium to float.				

3.2.2 Radioactive Tank 50 Waste Used

Approximately two liters of the Tank 50 sample, obtained in October of 2017, were used for radioactive testing, including analysis samples and contingency. Results from analyses of both the chemical and radionuclides of the waste sample can be found in Appendix E. The sample was taken at a height of 5 ½ feet from the tank bottom after the tank had been agitated using a single slurry pump for ~ 4.4 hours on Wednesday, October 18, 2017. Using a mixed sample obtained below the surface reduces the potential of collecting a surface layer of immiscible organic from the tank. The last full analysis [7.28] was done in the 3rd quarter of 2017 for a sample pulled on July 17, 2017.

3.2.3 Spike Material

Table 4 highlights the materials used to spike the test solutions to demonstrate the effect of those materials on the HGR. Actual masses of the spikes added to each reactor can be found in Appendix A, Table 13 and Table 14.

One of the spikes is Modular Caustic Side Solvent Extraction Unit (MCU) Solvent, locally referred to as "Scratch Blend." [7.29]. This material is a blend of Next Generation Solvent containing Isopar™ L; a

mixture of both BOBCalixC6 and MAXCalix, the Modifier, and trace amounts of two suppressors.[1] Another spike is BFS solids which is normally blended with grout-premix [7.30]. That is, grout-premix spike material is a mixture of BFS, Fly Ash, and Cement, which is used to make grout for Saltstone. A small addition to the grout-premix for some tests is called Admix, which is technically referred to as: Daratard™ 17 and is made of 30 to 50 wt% corn syrup, 30 to 50 wt% water, and 10 to 20 wt% calcium lignin sulfonate. The final additive is monosodium titanate (MST) that potentially contains residual organic contamination from manufacturing.

Table 4. Spike materials for both simulant and radioactive tests

Organic Spike Material	Target Amount in Simulant	Added Reagent (2)	TOC Contribution mg/L	Target (4) for Test mg	Approx. (5) in Test mg
Formate (1)	247 mg/L TOC	926 mg/L formate	247	24.7	25
MCU Solvent	11 ppm as Isopar™ L	15 ppm MCU Solvent (3)	14.6	1.5	4
Blast Furnace Slag	1000 mg/L	1000 mg/L BFS	Trace (6)	Trace (6)	Trace (6)
Grout-premix	2222 mg/L	2222 mg/L grout-premix	Trace (6)	Trace (6)	Trace (6)
Admix		0.75 mg / g-grout-premix	0.32	0.032	1
MST as-received	0.4 g MST/liter salt solution	Filtrate Only	Trace (6)	Trace (6)	Trace (6)

(1) In the form of sodium formate.
(2) Note that MCU Solvent is approximately 79 wt% carbon and Admix (Daratard™ 17) is approximately 19 wt% carbon.
(3) MCU solvent is nominally 75 wt% Isopar™ L.
(4) Target is based on 100 mL reactor simulant volume.
(5) Actual masses of spikes for Solvent and Admix are much larger than target because of the difficulty to add these small quantities.
(6) The organic content of these additions was not measured.

3.3 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

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[1] BOBCalixC6 is the extractant calix[4]arene-bis(*tert*-octylbenzocrown-6). MAXCalix is the extractant 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy) calix[4]arene-benzocrown-6. The Modifier is 1-(2,2,3,3-tetrafluoropropoxy),-3-[4-(*sec*-butyl)phenoxy]-2-propanol. The two suppressors are 1,3-dicyclohexyl-2-(isotridecyl)guanidine and tri-*n*-octylamine.

4.0 Results and Discussion

4.1 Pre-Test Evaluation: Shakedown

Before any testing with either simulant or Tank 50 waste began the reactors were tested to determine if they were leak tight and impermeable to H_2. The Run Plan [7.24, Table 2] included a series of shakedown tests, which are shown in Table 5. Note, the target temperatures in this, and all subsequent tables are what is listed in the approved Task Plan [7.24]; however, due to the internal temperature correction discussed in [2.4.1] the actual test temperatures are slightly different and indicated directly on each graph.

Table 5. Shakedown tests to baseline sealed reactors

Test #	Test Type	Nominal (1) Temperature °C	Start Pressure, psig	Fill Gas	Liquid	Amount of liquid, mL	Duration h
1	Leak Tests	120	10 to 25	Air, No H_2	None	Zero	>4
2	Standard H2	25	10 to 25	10 ppm H_2	None	Zero	>4
3	1 M NaOH	50	10 to 25	N_2, No H_2	1 M NaOH	180	>4
4	Al pellet – 150 μg	50	10 to 25	N_2, No H_2	1 M NaOH	180	>4
5	1 M NaOH	120	10 to 25	N_2, No H_2	1 M NaOH	100	>4
6	Al pellet – 750 μg	120	10 to 25	N_2, No H_2	1 M NaOH	100	>4

Note (1): Nominal is ±5°C.

All the results for these six shakedown tests are located and described in detail in Appendix F. Those results showed that the reactors had no leaks during the pre-shakedown leak checks with using helium, and then during Test 1 with air, held at 120°C. Furthermore, these tests demonstrated that the reactors are impermeable to H_2, which is a less permeable gas than helium. For Test 2, when a known mass H_2 was introduced into the reactors, it was accurately measured after heating and sampling, which demonstrated the reactors to be leak tight.

For Test 3, when heating a measured mass 1 M NaOH, i.e., caustic, in the reactors with a 20-mL head space (which was actually ~17 mL due to the volume of the stir bar), there was a measurable, but a small amount of H_2. The H_2 measured in Test 3 was subsequently found to be from tramp material in the caustic [7.25]. When the head space was made larger in Test 5, i.e., 100 mL (which was actually ~97 mL due to the volume of the stir bar), the H_2 was no longer detectable. On introducing aluminum into the sealed reactors with caustic, the H_2 produced was accurately measured. When the mass of caustic increased, subsequently reducing the head space, the measured H_2 was slightly lower than estimated This is assumed to be due to H_2 being absorbed into the liquid.

In general, these shakedown tests demonstrated a maximum HGR of 4 x 10^{-9} (ft^3/h)/gal; therefore, longer-duration tests were planned for simulant and radioactive waste tests to pursue lower LOD.

4.2 <u>Tank 50 Simulant Tests</u>

Simulant testing included four planned campaigns, after which a fifth was included to repeat some tests with important spikes over a 6-day period, instead of the 4 hours used for most of the simulant tests. The goals of simulant testing were: (1) to perfect operations before starting radioactive work, (2) have a good idea of HGR with and without spikes, and (3) to demonstrate measurements of HGR at a LOD as low as 1.0×10^{-10} (ft^3/h)/gal. Before discussing the simulant test results, the report provides analytical data from all the liquid samples pulled from the reactor after each test. Note, the word "Simulant" means a simulant of Tank 50 waste as shown in Table 3 and will be used alone from hereafter.

4.2.1 Analytical data from simulant tests

Table 6 shows the analytical results from the simulant samples after each test when samples were pulled. The most distinctive aspect of the results is that there seemed to be an absence of a trend in the chemical make-up, be it spike material (no Spike, BFS, or grout-premix, shown in Table 4), temperature (50°C to 120°C); duration (4 hours to 6 days), etc. That is, it appears that none of the spikes, temperatures, or durations had a significant impact of the chemical make-up of the waste. The simulant control (no spikes)[2] tests (in yellow blocks) had 61 ±32 mg/L of Total Organic Carbon (TOC), which is assumed tramp material, previously discussed, from the sodium hydroxide used to make the simulant. The formate spike had a target TOC concentration of 247 mg/L and it turned out to have an average concentration of 294 ±17 mg/L (in blue boxes). When considering the tramp TOC, the average formate TOC results is 294 – 61 = 235 mg/L, which matches the target of 247 mg/L within measurement uncertainty.

Table 6. Analytical data for samples pulled during simulant testing

Test No.	Plan Table#	Reactor #	Simulant Spike Type	(A)noxic (O)xic	Target (4) Temp./Dur.	ADS No.	TIC mg/L	TOC mg/L	Free OH M	Nitrite mg/L	Nitrate mg/L	Sulfate mg/L	Formate mg/L	Aluminum mg/L	Sodium mg/L
Pre	4	NA (1)	Pre-Test Simulant	O	20°C / NA	8545	3320	66.8 (2)	1.84						
Pre	4	NA	Pre-Test Simulant	O	20°C / NA	8546				29300	120000	4600		4090	117000
2	5	HGV-2	Formate-Spike	A	100°C / 4 h	8662	3540	308 (3)	1.88	29200	120000	4610	1060	4180	123000
2	5	HGV-4	Formate-Spike	O	100°C / 4 h	8661	3520	308	1.88	29200	124000	4670	1060	4170	123000
2	5	HGV-5	Formate-Spike	O	100°C / 4 h	8660	3840	272	1.85	28900	115000	4630	1050	4120	121000
3	6	HGV-2	Grout-Spike	O	100°C / 4 h	8887	3360	97.6	1.83	31200	122000	5250		3930	122000
3	6	HGV-4	Grout+Admix	O	100°C / 4 h	8888	3370	111	1.81	31100	128000	5050		3960	123000
3	6	HGV-6	MCU-Spike	O	100°C / 4 h	8889	3350	85.2	1.85	31200	128000	5020		4270	123000
3	6	HGV-8	Control - None	O	100°C / 4 h	8890	3400	103	1.84	31700	130000	5090		4270	124000
4	7	HGV-2	BFS-Spike	A	100°C / 4 h	8807	3460	111	1.83	31600	116000	5320		4340	129000
4	7	HGV-4	BFS-Spike	O	100°C / 4 h	8808	3240	28	1.76	31400	109000	5160		3990	118000
4	7	HGV-6	MST-Spike	O	100°C / 4 h	8809	3240	28	1.69	31700	110000	5090		4050	116000
4	7	HGV-8	Control - None	O	100°C / 4 h	8810	3280	28	1.79	32500	112000	5190		4110	119000
5	8	HGV-2	Grout-Spike	O	100°C / 6 days	9044	3360	42.4	1.81	30000	122000	4870		3640	118000
5	8	HGV-4	Formate-Spiked	O	100°C / 6 days	9045	3110	288	1.82	29800	122000	4790	954	3880	118000
5	8	HGV-6	MCU-Spiked	O	100°C / 6 days	9046	3360	44	1.71	29900	122000	4790		3920	118000
5	8	HGV-8	Control - None	O	100°C / 6 days	9047	3420	44.8	1.87	29400	120000	4740		3920	119000
(1) NA = Not Applicable				Average =			3386	NA (4)	1.82	30506	120000	4929	1031	4053	120688
(2) Yellow data = TOC of simulant without any				Standard Deviation =			162	NA (4)	0.06	1153	6250	244	52	179	3400
spike. See discussion below table.				%rsd =			5	NA (4)	3.05	4	5	5	5	4	3
(3) Blue data = TOC of simulant with Formate.															
See discussion below table.				Minimum =			3110	28	2	28900	109000	4600	954	3640	116000
(4) TOC was changed as part of testing, i.e., NA				Maximum =			3840	308	2	32500	130000	5320	1060	4340	129000

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[2] For the tests described in this report "control" refers to sealed reactors that contained simulant or Tank 50 waste with no spike material. These terms are interchangeable throughout the report.

4.2.2 Overall Simulant Test Results

The simulant testing included 5 tests. However, Test 1 was broken up into 3 subtests: (1) an anoxic head space, which used nitrogen, (2) an oxic head space, which used H_2-free air, and (3) an oxic head-space but with a duration of 6 days, as opposed to 4 hours for most of the other tests. Those subtests and along with each of the individual tests will be discussed in detail in Appendix G. In this section, the results are summarized.

One of the goals of the simulant tests was help define protocols for the subsequent radioactive tests, by testing with a range of paraments, i.e., spike material, reactor head space, temperature, duration, etc. Table 7 shows all the H_2 generated test data, in ppm, and parameters used. Table 8 shows the data for the same tests, but in terms of HGR. Note that for the HGR calculation, the sampling initial pressure (close to 20 psig) and temperature (usually between, 22°C to 28°C), were adjusted to 1 atm (14.7 psia) and 25°C.

Table 7. H₂ generated from simulant tests

Test No.	Type atm	Temp. °C	Head mL	At Temp. hours	No Spike ppm	Formate ppm	BFS ppm	Grout-premix ppm	Grout-premix+ Admix ppm	MST ppm	Solvent ppm
1	Anoxic	113.6	90	4.5	6.1						
1	Oxic	21.9	10	25	1.0						
1-2	Oxic	115.0	90	4.7	24.4						
1-2(6d)	Oxic	23.7	10	181	7.8						
2	Anoxic	93.4	90	5.2		3.0					
2	Oxic	93.4	90	5.2	3.2	4.1					
3	Oxic	94.4	90	4.4	6.3			6.7	96.0		4.6
4	Anoxic	93.9	90	4.9			2.7				
4	Oxic	93.9	90	4.9	3.3		4.6			2.7	
5	Oxic	94.5	90	148	37.5	47.5		30.1			39.9

Table 8. HGR from simulant tests

Test No.	No Spike (ft³/h) /gal	Formate (ft³/h) / gal	BFS (ft³/h) / gal	Grout-premix (ft³/h) / gal	Grout-premix + Admix (ft³/h) / gal	MST (ft³/h) / gal	Solvent (ft³/h) / gal
1 (N₂)	4.5E-07						
1 (Air)	1.3E-09						
1-2	1.5E-06						
1-2(6d)	1.3E-09						
2		1.9E-07					
2	2.1E-07	2.6E-07					
3	4.9E-07			5.1E-07	7.4E-06		3.5E-07
4			1.9E-07				
4	2.3E-07		3.0E-07			1.9E-07	
5	7.5E-08	1.0E-07		6.0E-08			8.4E-08

This large range of parameters makes it difficult to pick trends for data with similar parameters; therefore, the results will only be summarized here. For a more comprehensive understanding of the data, a description of each individual test is described in Appendix G. The predominant trend is with temperature,

which is best illustrated with the no-spike data. Figure 13 depicts those data points, which clearly show that the HGR increases as temperature increases. However, because the LOD for H_2 was 1 ppm and the LOQ was 3 ppm, some of the data are either barely, or not quantifiable, as seen in Table 7. Furthermore, the H_2 measured came principally from tramp material subsequently found in the caustic used to make up the simulant [7.25].
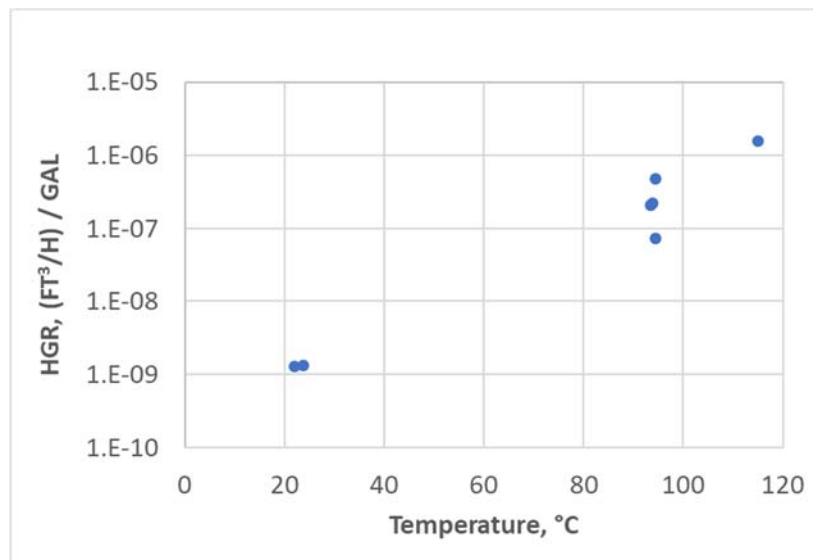
Figure 13. HGR of all simulant data without spike material

In summary, the simulant tests demonstrated the following. For reactors that were held above 110°C for approximately 5 hours, which were, Test 1-1 with a nitrogen-filled head space, and Test 1-2, with a H_2-free air-filled head space, the H_2 produced into the oxic atmosphere was approximately 3.5 times greater than that into the anoxic atmospheres. For the 6-day test (which actually was 7.5 days long), at room temperature, the measured HGR was approximately 1.3×10^{-9} $(ft^3/h)/gal$. In Test 2, spiked with formate and held at 93°C for approximately 5 hours, H_2 was detected, but barely quantifiable, and was similar to the reactor that had no-spiked simulant. Furthermore, the anoxic and oxic atmospheres did not produce the significant different results found from Test 1. For Test 3, which had a variety of different spikes and that was held at 94°C for approximately 4 hours, the results were similar to those of Test 2, except for the two reactors that contained Admix. For those reactors, the grout-premix spike was joined with a lignin organic spike (Admix) and resulted in producing significant H_2 of about 17 times larger than the no-spike simulant or those that only had grout-premix and solvent spikes. For Test 4, which also had a variety of spike and was the last short-term test held at 94°C of approximately 5 hours, the results showed no surprises. The spikes of BFS or MST did not produce H_2 larger than what was obtained from the no-spike simulant where the H_2 was barely quantifiable. From these 4-hour duration results a final longer-term test was performed. Test 5 was held at 94°C for approximately 6 days. The H_2 produced was measurable but it was equivalent to that produced in the no-spike simulant. The reactors had HGR of approximately 3×10^{-8} $(ft^3/h)/gal$.

Note that because the H2 production was insignificant when adding spikes of MST, formate, and MCU solvent they were not included in the next phase of testing, i.e., radioactive Tank 50 waste. Furthermore, after reviewing the results with the addition of the Admix spike it, too, was not included in radioactive testing, with concurrence from the customer, because the use of Admix is currently prohibited in the facility by the DSA.

4.3 Radioactive Tank 50 Waste Tests

The initial version of the run plan for radioactive testing included five planned campaigns with an oxic head space. However, after evaluating the safety documentation it was necessary to include an initial test with an anoxic head space, as in the simulant testing, to quantify the H_2 produce to demonstrate that the lower flammability level (LFL) would be exceeded; therefore, the run plan was revised [7.24]. The revision also included a final test added to repeat some important tests over a longer period (6 days) then the 16 hours that most of the radioactive tests utilized. Before discussing the H_2 generation results, the analytical data from all the liquid samples pulled from the reactors after each test are shown in the next section.

4.3.1 Radioactive Tank 50 Waste Analytical data

Table 9 shows the analytical results from the radioactive waste samples. The most distinctive aspect of the results is the absence of trend in the chemical make-up of the waste despite the variation in testing parameters be it, spike material: none, BFS, or grout-premix, temperature: 50°C to 120°C, duration: 16 hours to 6 days, etc. The highest silicon concentration occurred at the lowest temperature of 50°C for BFS and grout-premix, additives which contain silicon, as may be expected since higher temperatures promote silicate formation. However, the spread in the data indicates no statistically significant claim for that suspected behavior. In summary, none of the temperatures, spikes, or durations had a statistically discernible impact of the chemical make-up of the waste.

Table 9. Analytical data from each reactor after each test

Test #(1)(2) New (Old)	Plan (1) Table#	Reactor #	Tank 50H Waste Spike Type	(A)noxic (O)xic	Target (3) Temp./Dur.	TS # (4) TS200-18-	ADS No.	TIC mg/L	TOC mg/L	Free OH M	Oxalate mg/L	Nitrite mg/L	Nitrate mg/L	Sulfate mg/L	Formate mg/L	Al mg/L	Cr mg/L	K mg/L	Na mg/L	Si mg/L
1 (1A)	9	HGV-2	Control - None	A	120°C / 16 h	A-02011	9345	3180	268	2.33	473	27800	117000	4590	241	4270	43.5	773	91500	85.3
1 (1A)	9	HGV-3	BFS	A	120°C / 16 h	A-02012	9346	3200	268	1.98	467	26500	111000	4440	235	3950	34.6	653	87300	62
1 (1A)	9	HGV-4	Grout	A	120°C / 16 h	A-02013	9347	3220	268	2	480	27400	115000	4510	241	3940	24.5	780	88100	74.3
2 (1B)	10	HGV-2	Control - None	O	120°C / 16 h	A-02035	9378	3140	252	2.03	470	27400	115000	4440	235	4380	98.4	725	87300	57.6
2 (1B)	10	HGV-3	BFS	O	120°C / 16 h	A-02036	9379	3140	252	1.93	492	28300	119000	4600	247	4300	68.7	739	88000	57.7
2 (1B)	10	HGV-4	Grout	O	120°C / 16 h	A-02037	9380	3100	252	1.92	439	25100	105000	4040	220	4170	86.3	775	87400	56.5
3 (2)	11	HGV-2	Control - None	O	120°C / 16 h	B-02064	9530	3060	267	1.92	615	26600	111000	4360	235	4490	62.2	450	123000	61.1
3 (2)	11	HGV-3	BFS	O	120°C / 16 h	B-02065	9531	3090	254	1.98	585	26400	110000	4370	225	4090	55.8	503	122000	60.5
3 (2)	11	HGV-4	Grout	O	120°C / 16 h	B-02066	9532	3140	262	1.97	602	26700	111000	4330	231	4230	55.1	559	123000	60.7
4 (3)	12	HGV-2	Control - None	O	75°C / 16 h	B-02073	9533	3060	248	1.96	895	26200	110000	4220	190	4760	52.9	434	123000	118
4 (3)	12	HGV-3	BFS	O	75°C / 16 h	B-02074	9534	3060	248	1.95	557	26300	109000	4210	216	4400	49.3	434	114000	116
4 (3)	12	HGV-4	Grout	O	75°C / 16 h	B-02075	9535	3060	248	1.94	542	25900	107000	4100	212	4320	53	520	116000	128
5 (4)	13	HGV-2	Control - None	O	50°C / 16 h	C-02145	9663	3370	158	1.89	513	27200	123000	4360	218	4430	49.7	501	116000	77.1
5 (4)	13	HGV-3	BFS	O	50°C / 16 h	C-02146	9664	3370	142	1.83	515	27100	122000	4320	217	4460	49.8	563	116000	155
5 (4)	13	HGV-4	Grout	O	50°C / 16 h	C-02147	9665	3360	142	1.91	519	26800	120000	4250	217	4520	50.4	618	118000	159
6 (5)	14	HGV-5	Control - None	O	35°C / 26 days	B-02152	9688	3390	251	1.93	245	27500	116000	4540	234	4670	57.2	437	125000	31.6
6 (5)	14	HGV-6	Control - None	O	35°C / 26 days	B-02153	9689	3410	254	1.87	233	27000	114000	4380	234	4350	53.2	432	119000	27.9
7 (6)	15	HGV-2	BFS	O	75°C / 6 days	C-02189	9935	3330	140	1.89	521	27900	125000	4370	219	4580	68.7	473	126000	35.1
7 (6)	15	HGV-3	Grout	O	75°C / 6 days	C-02190	9936	3370	143	1.84	524	27400	117000	4370	219	4290	57.4	511	122000	85.3
7 (6)	15	HGV-4	Control - None	O	75°C / 6 days	C-02191	9937	3380	146	1.89	524	27400	122000	4250	218	4460	64.7	511	118000	30.7
7 (6)	15	HGV-5	BFS	O	75°C / 6 days	C-02192	9938	3380	142	1.84	523	27600	123000	4290	223	4390	60.7	519	116000	30.5
7 (6)	15	HGV-6	Grout	O	75°C / 6 days	C-02193	9939	3390	142	1.86	522	26400	121000	4270	219	4170	57.4	521	125000	30.5

(1) New test & table #s from Test Plan SRNL-L3100-2017-00123, R. 1						Average =		3236	NA(5)	1.9	512	26950	115591	4346	225	4346	57	565	111436	73
(2) Old test #s from Test Plan SRNL-L3100-2017-00123, R. 0						Stand. Dev =		137	NA	0.1	126	743	5787	142	13	207	15	121	14915	40
(3) Actual temp. & times are slightly different from Test Plan target						%rsd =		4	NA	5.3	25	3	5	3	6	5	27	22	13	55
values. They can be found in the results section of this report.																				
(4) TS = Treatability Study, defined in SRNL Proc. Manual L1, Proc. 6.04						Minimum =		3060	140	1.83	233	25100	105000	4040	190	3940	24.5	432	87300	27.9
(5) NA = Not Applicable. TOC was changed as part of testing.						Maximum =		3410	268	2.33	895	28300	125000	4600	247	4760	98.4	780	126000	159

4.3.2 Overall Tank 50 Test Results

The radioactive tests were limited to 5 sealed reactors because two were held in reserve in case further simulant testing would be necessary. Of the seven-planned radioactive tests, the first five only used three reactors because two reactors were used for a sixth, long-term, test, i.e., 26 days, that continued while all other tests were ongoing. To have a better comparison for the added spikes, the first five tests had the same operating parameters except the temperature, which ranged from 120°C down to 50°C. When the long-term test was completed a final, seventh, test was performed with all five reactors at the important temperature point of 75°C. This temperature is the maximum assumed by a flammability analysis [7.31] included as part of the Saltstone Facility DSA [7.32].75°C

The details of each individual test are discussed in Appendix H. This section discusses the overall observations. Table 10 lists the data H_2 generation in order of temperature. The data are graphically depicted in Figure 14. As the uncertainty analysis determined, Section 4.4, the addition of solids (i.e., BGS or grout-premix) increases the H_2 production. Within statistical uncertainty (at 95% confidence – see Appendix J) there is no discernible difference between the increase due to BGS or grout-premix. This can be better seen in the HGR results shown in tabular form in Table 11 and graphically in Figure 15. To illustrate the impact of the ±7% uncertainty (discussed in Section 4.4), it is shown on both graphs, but only for the No Spike (Oxic) data so that all the data can be clearly seen. Note that the bold values seen in Table 10 and Table 11 for BFS and grout-premix for the 144-hour test indicate the average of the results from two reactors. That test, which used 5 reactors, included two replicate tests for each spike. The results for each of the two replicates were very similar and well within measurement uncertainty. Note that for the HGR calculation, the sampling initial pressure (usually close to 20 psig), and temperature (usually between 22°C to 28°C) were adjusted to 1 atm (14.7 psia) and 25°C.

Table 10. H₂ concentration measured values from radioactive-waste Tests 1-7

Type	Temp.	Time at Temp	No Spike	BFS	Grout
atm	°C	hours	ppm	ppm	ppm
Oxic	31.7	333	16.96		
Oxic	32.3	643	46.36		
Oxic	32.3	643	13.48		
Oxic	49.1	16	Below DL	1.59	1.42
Oxic	72.4	16	1.39	5.94	6.81
Oxic	71.6	91	12.73	18.25	37.53
Oxic	71.5	144	23.01	**26.73**	**39.31**
Oxic	95.0	16	16.62	32.22	45.26
Oxic	113.2	16	74.05	86.22	175.85
Anoxic	114.9	16	69.34	132.51	163.38
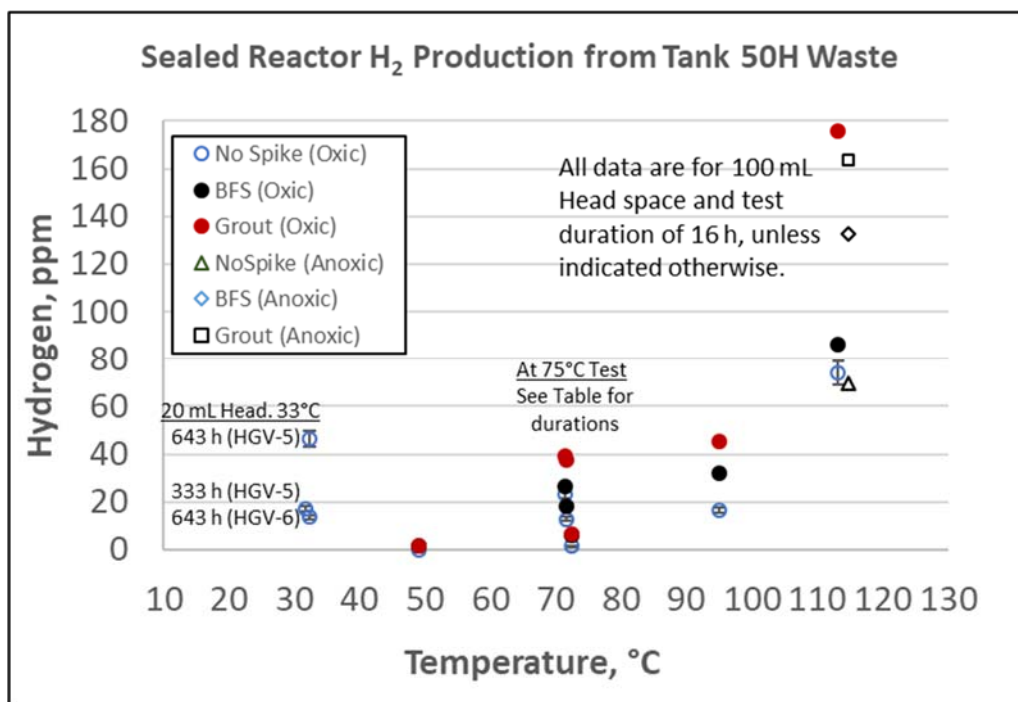
Figure 14. H₂ measurements from radioactive-waste Tests 1-7

Table 11. HGR measurement values from radioactive-waste Tests 1-7

ATM	Temp.	Time at Temp	No Spike	BFS	Grout-premix
	°C	hours	(ft³/h) / gal	(ft³/h) / gal	(ft³/h) / gal
Oxic	31.7	333	1.73E-09		
Oxic	32.3	643	1.87E-09		
Oxic	32.3	643	7.66E-10		
Oxic	49.1	16	Below DL	2.61E-08	2.36E-08
Oxic	72.4	16	2.21E-08	9.84E-08	1.14E-07
Oxic	71.6	91	4.58E-08	6.01E-08	1.33E-07
Oxic	71.5	144	4.86E-08	**4.92E-08**	**8.80E-08**
Oxic	95.0	16	2.86E-07	5.63E-07	8.01E-07
Oxic	113.2	16	1.42E-06	1.74E-06	3.56E-06
Anoxic	114.9	16	1.36E-06	2.57E-06	3.40E-06
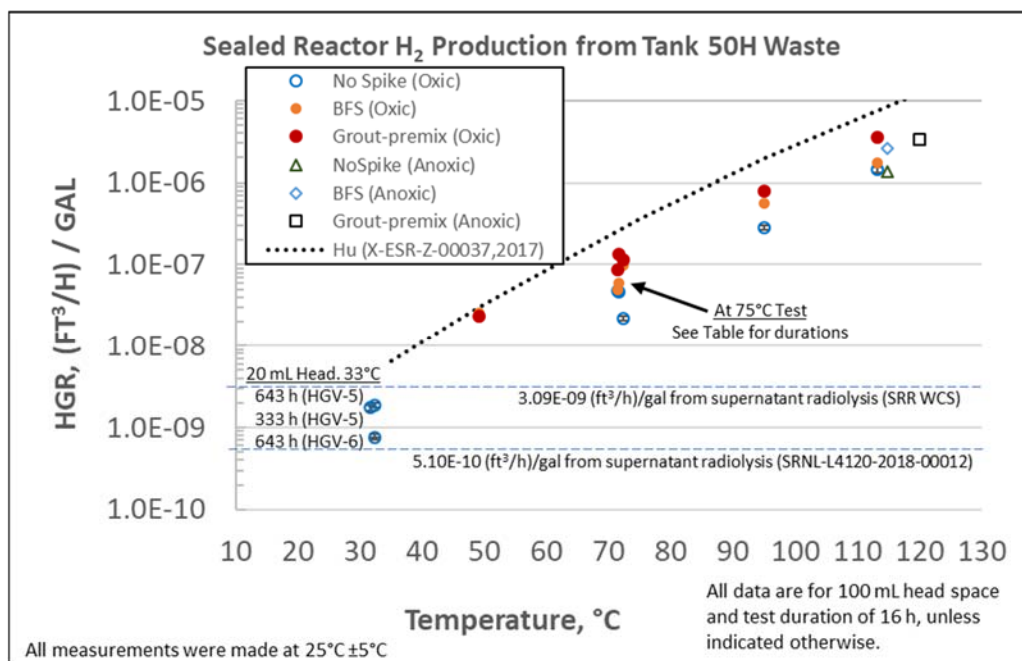
Figure 15. HGR measurements from radioactive-waste Test 1-7

From these 7 tests, the difference in the rate of production of H_2 for an overlaying oxic or anoxic atmosphere is statistically insignificant; a result which differs from Test 1 of the simulant test. Figure 15 shows that the HGR production is exponential with temperature and appears linear on a logarithmic scale. When considering the presence of BFS and grout-premix, the HGR increases, with the grout-premix test at 115°C having the largest rate of 1.0×10^{-6} (ft^3/h)/gal. Statistical analysis (Appendix J) indicates no significant discernible difference in rates between BFS and grout-premix. Furthermore, all the experimental HGR results are bounded by the calculated HGR based on the Hu equation adjusted to a 25°C [7.33], employing Tank 50 characterization data shown in Appendix E, Table 20. As was previously done (see Equation 3 of reference [7.34]), the TOC and Al values from the radioactive Tank 50 characterization were input into the Hu equation and the resulting HGR was calculated at various temperatures in units of mol/day/kg. These results were then converted to units of (ft^3/h)/gal at 25°C (the nominal sampling temperature for these experimental tests). The TOC value used 273 mg/L carbon which gives a TOC of 2.21×10^{-2} wt% using a density of 1.237 g/mL; the Al value used is 5,040 mg/L which gives an Al of 0.407 wt% using a density of 1.237 g/mL.

Also shown on Figure 15 is the result for the long-term test that lasted over 26 days (643 hours). The temperature was held at 33°C to obtain a radiolytic result and the Tank 50 Waste averaged HGR of $1.32 \times 10^{-9} \pm 0.14 \times 10^{-9}$ (ft^3/h)/gal. This HGR result is significantly below the estimated SRR Waste Characterization System (WCS) radiolytic values of 3.09×10^{-9} (ft^3/h)/gal for supernatant and 5.08×10^{-9} (ft^3/h)/gal for slurry (Appendix I), which means the estimates are conservative. Furthermore, this HGR result matches, within uncertainty, the Monte Carlo n-Particle Code [7.14] estimate of radiolytic rate of 5.1×10^{-10} (ft^3/h)/gal from a 180-mL batch of waste, as used for this 26-day test.

Another way of looking at the HGR data is by using the Arrhenius methodology to obtain the activation energy, E. Equation (2) is referred to as the Arrhenius equation [7.35]

$$k = A \bullet e^{-E/RT} \qquad (2)$$

where k = Rate Constant, i.e., HGR, A = frequency factor constant, E = Activation Energy, R = Universal Gas Constant, and T = Absolute Temperature.

In logarithmic space Equation (2) can be written as $\ln[HGR] = (-E/R)(1/T) + \ln[A]$; so, plotting the log of HGR versus the reciprocal of temperature provides a slope of -E/R and thereby the activation energy, E. A full description of using the results with Equation (2) is given in the Uncertainty Analysis, Appendix J; however, when putting the data given in Table 11 into the form of Equation (2) the results are shown in Figure 16.
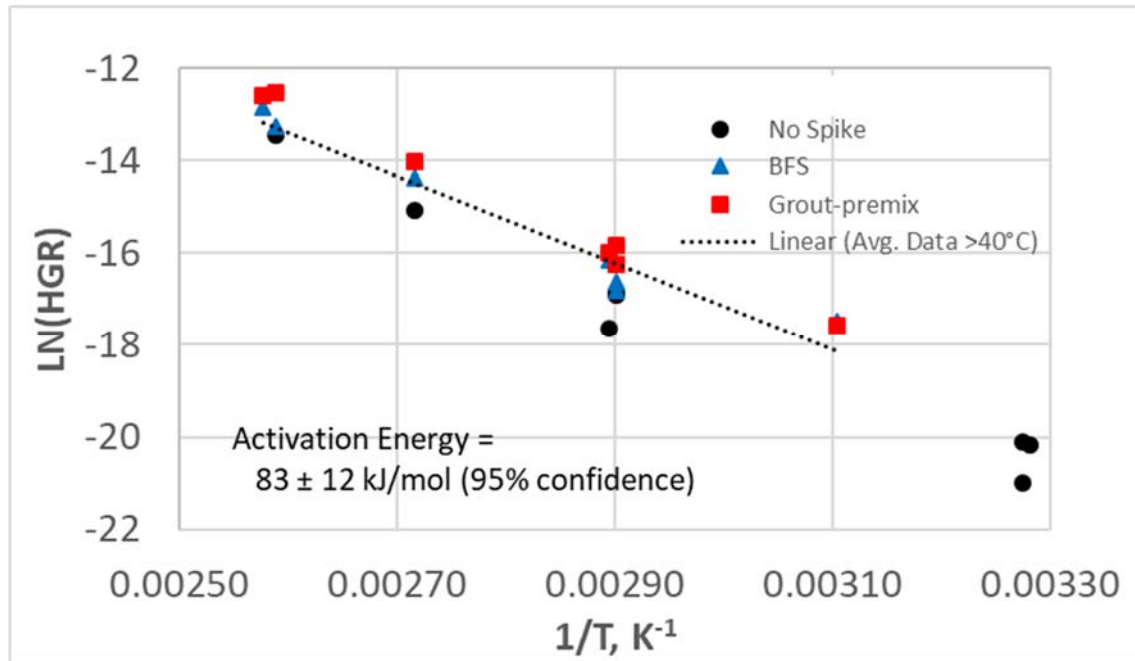
Figure 16. HGR measurements from radioactive-waste Test 1-7

Only an average slope is shown in in Figure 16, because of the three sets of data (BFS spike, grout-premix spike, and no spike), the slopes are indistinguishable when considering a 95% confidence level. Note that this average slope excluded data from Test 6, which was done at 32°C to measure the radiolytic HGR. That is, the slope of the line shown in Figure 16 is for the thermolytic HGR as well as the value of activation energy shown, i.e., 83 kJ/mol. Furthermore, a linear slope on an Arrhenius plot implies the reaction is not complex, in this case, the release of H_2 from the liquid waste. However, while the slopes are the same for results of the individual spike data, note that all the no-spike data fall <u>below</u> the other two sets of spiked data. The statistics indicate that while the slope of the no-spike data is not different from that of BFS or grout-premix many of the intercepts of those data, i.e., ln[A], are different. This implies that the addition of either BFS or grout-premix does increase H_2 production.

4.3.3 H₂ Generation from Oxic Versus Anoxic Atmospheres

As is discussed in the Uncertainty Analysis, Appendix J; a single radioactive test using an anoxic head space implies there is a difference in H_2 generation when waste contains BFS and grout-premix. However, the data are challenging to interpret. They show that between the grout-premix and No-Spike results there was *no significant difference* in the HGR; however, there *was a significant difference* between both BFS

and grout-premix HGRs, and the BFS and No-Spike HGRs. Because there was only a single test performed with an anoxic atmosphere, then that test would have to be repeated to confirm the results.

4.3.4 Comparison of Test Durations and Simulant versus Radioactive Waste Results

In performing all the testing, an open question was how long should a test be held at a target temperature to obtain an accurate result. One concern relative to the short duration test deals with the fraction of time required for cooling and how much additional H_2 is generated at these conditions. For a short reaction period of 4 hours, the amount of additional H_2 formed when cooling over 16 hours at gradually declining temperature may prove appreciable and bias the determined HGR high. Another consideration is that short reaction times lead to low total H_2 formation and concentrations nearer the GC method LOD. Hence, the potential exists to experience high data variance for shorter reaction periods. For the convenience of shift work, the initial period for the simulant work was 4 hours. However, the time period was eventually thought too short due to the duration associated with bringing the reactors to steady state, followed by cooling the reactors and then pulling the samples. Hence, radioactive testing moved to holding the reactors at the target temperatures for 16+ hours. Eventually, several heating durations were used, which should help to better understand this aspect of testing.

The data in Figure 17, Figure 18, Figure 19, Figure 20, have been plotted as a function test duration to illustrate the importance of longer-term tests. The durations for the 'isothermal' period ranged from 4 hours to 26 days. From Figure 17 and Figure 19, it appears the 4-hour tests were too short for accurate quantification, probably because of the significant heat-up and cool-down periods as compared to the heating period. The results of the longest period, 650 hours, appears to be equivalent to that at 180 hours. At 16 hours, the values approach the long-term data although results for the control samples in Figure 18 are less satisfactory. The 6-day period (144 hours) is probably the optimum for such tests where the heat up and cool-down periods are approximately 10% of the steady-state heating period.
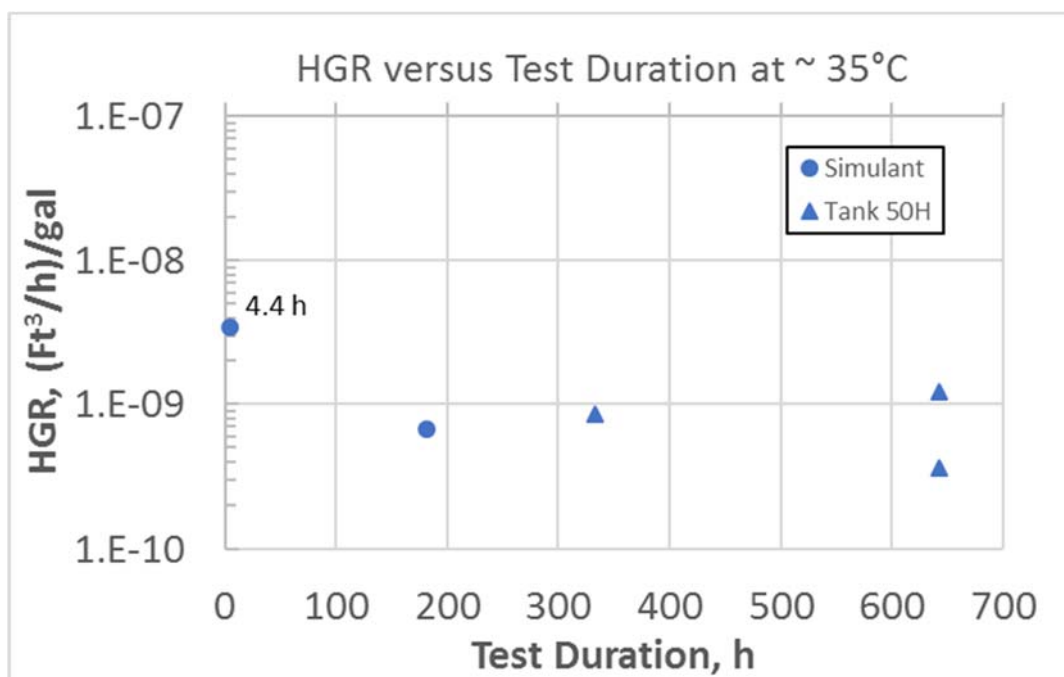
Figure 17. Duration throughout no-spike testing at approximately 35°C
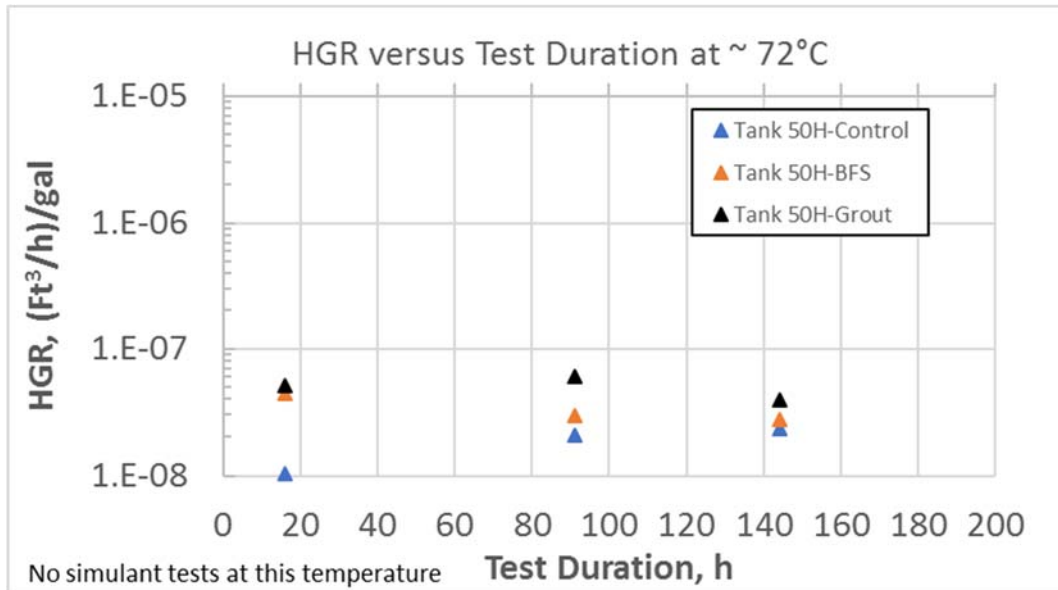
Figure 18. Duration throughout testing at approximately 72°C
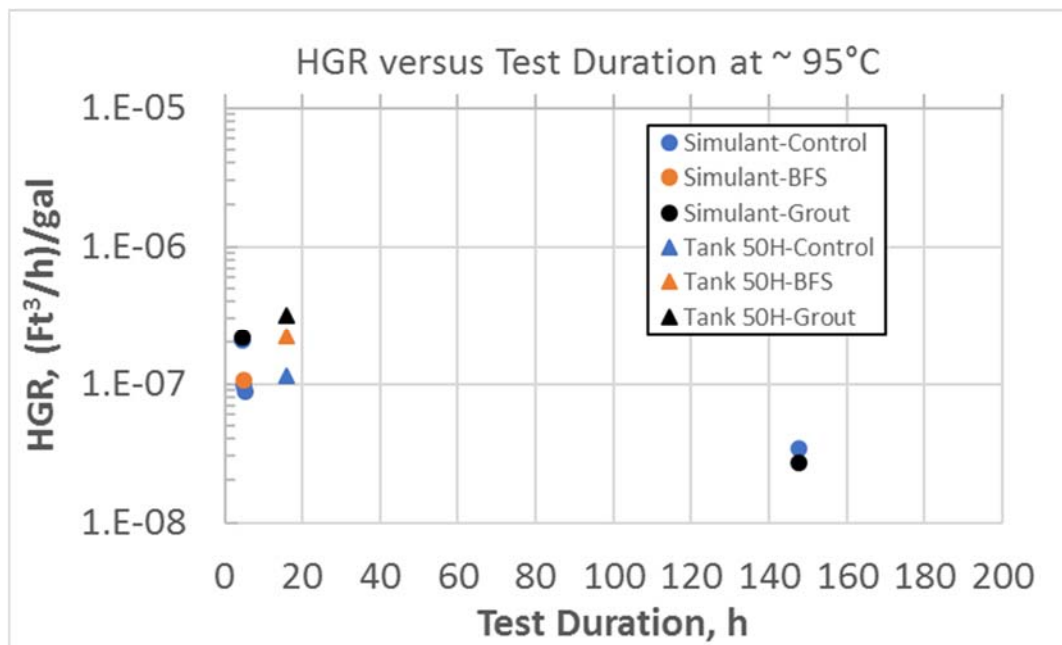
Figure 19. Duration throughout testing at approximately 95°C
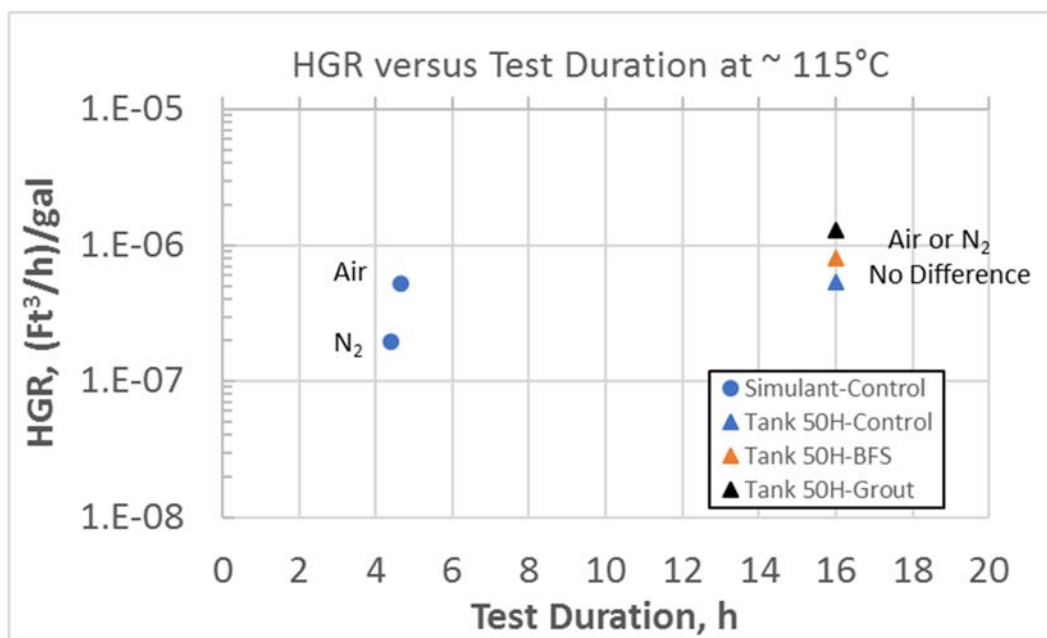
Figure 20. Duration throughout testing at approximately 115°C

4.4 Measurement Uncertainties

Appendix J contains the uncertainty analyses for the measurements and calculations made for the radioactive tests. Besides the analytical measurements made on liquid samples, the principal measurements were temperature, pressure, reactor waste volume, reactor head space volume, masses added, and time. The uncertainties for each can be found in the Instrument list in Appendix B. The uncertainty of the principal calculation of HGR ranged from 3 to 10 %RSD, for a confidence level of 95%. The average %RSD = 4.3 for the entire set of radioactive waste tests, shown in Table 39 and Table 40. The largest contributor to the HGR uncertainty was from the GC H_2 measurement followed by temperature. However, the HGR are reported with ±2 standard deviations in the variability of the H_2 measurements, which is generally larger that ±4.3% RSD and close to ±7%. For all the H_2 and HGR results discussed in the appendices the size of the data points generally is larger than this uncertainty.

4.5 Other Possible Gasses in Off-gas

The off-gas from the vessels was analyzed on a molecular sieve 5A (MS-5A) column with argon carrier +gas. The instrument method was optimized for H_2; however other permanent gases could potentially be detected and quantified with modifications of the method. Per discussion with the vendor, polar gases or gases heavier than ethane will not make their way through the MS-5A column. Thus, gases identified in Saltstone flammability evaluations [7.31], with the exception of H_2 (ammonia, benzene, butanol, Isopar™ L, Isopropanol, methanol, Norpar™, toluene, xylene) would not be detected in the SRNL testing. However, other gases of interest – methane and ethane could potentially be detected.

Chromatograms from samples at the highest targeted temperatures were manually examined to look for the potential evidence of presence of methane or other species. As described above, there were two sets of tests, one set with a nitrogen headspace and one set with a headspace of 20% oxygen, 0.5% krypton, balance nitrogen. No unidentified peaks were observed in the tests with the oxygen/krypton/nitrogen headspace.

However, krypton eluted at the end of the nitrogen peak, likely interfering with any potential ethane or methane.

The samples from the nitrogen headspace tests suggest other gases may be present but with very low certainty. See Figure 21 for chromatograms from Tank 50 waste, Tank 50 with BFS, and Tank 50 with grout-premix held at 115°C and 16 hours. It should be noted that this temperature exceeds maximum Tank 50 processing and maximum Saltstone curing temperatures. A small shoulder/bump can be seen on the Tank 50/grout-premix sample at 70 seconds and all three samples appear to have a bump at about 75 seconds. The bump at 70 seconds was not observed in calibration or room air gas samples, suggesting it is indeed a product of the testing. The bump at 75 seconds was seen in a room air sample but not in calibration gas samples, suggesting this may be an impurity associated with air or nitrogen.

Both bumps are too small for integration by the software. Without methane and ethane standards, these bumps cannot be positively attributed to either gas. However, it is known that methane and ethane elute after nitrogen.

Additional testing with higher concentrations of the additives at higher temperatures could possibly increase the concentration of the unknown species, which, along with additional gas standards and GC method modifications, could help with identification.
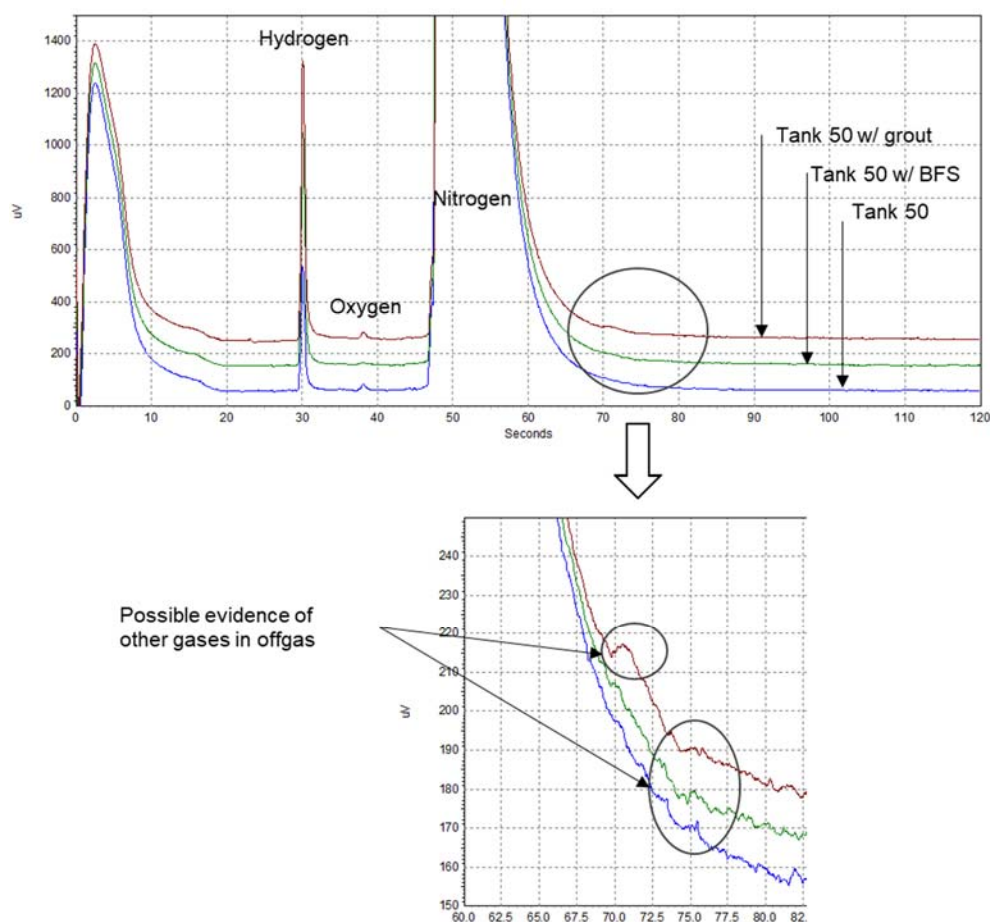
Figure 21. Sample Chromatograms of Tank 50, Tank 50 with BFS, and Tank 50 with grout-premix Showing Other Potential Gases

5.0 Conclusions

The equipment shakedown tests demonstrated the designed sealed reactor could adequately and accurate measure HGR. These tests provide the following highlights.

- Pre-test pressure evaluation of the reactors found no leaks when using helium, which demonstrated that the reactors are impermeable to H_2, which is a less permeable gas.
- A known mass of H_2 introduced into the reactors was accurately measured after heating and sampling thus confirming the reactors to be leak tight.
- Tramp organic species in the sodium hydroxide produced H_2 which limited the lowest quantification achievable for any examined additives.
- Shakedown testing with caustic demonstrated a HGR lower limit of quantification (LOQ) ~ 4 x 10^{-9} (ft^3/h)/gal; therefore, longer-duration tests were planned for simulant and radioactive waste tests to pursue lower LOQs.

The second phase of testing used non-radioactive simulant of Tank 50 waste and various additives. The findings include the following.

- A test with simulated Tank 50 samples at 115°C ± 5°C (for 4.7 hours) under an air atmosphere showed a measurable increase in HGR compared to a test blanketed by nitrogen.
- At 24°C ± 3°C (for 7.6 days), the HGR was approximately 7 x 10^{-10} (ft^3/h)/gal, demonstrating the ability to achieve measurements at the targeted sensitivity.
- Tests at 93°C ± 7°C (for 5.2 hours) with formate added at prototypical concentrations showed no statistically discernible H_2 production above the background attributed to tramp organics in the caustic simulant.
- Tests at 94°C ± 4°C (for 4.4 hours) containing grout-premix and a lignin organic spike (Admix) produced markedly more H_2. Upon review of the data, and given that Admix is currently prohibited from use in SPF, testing with Admix was discontinued.
- Manufacturing of MST may leave residual organics that could contribute to thermolytic generation of H_2 in Tank 50 and downstream processing. Tests exposing Tank 50 simulant at 94°C ± 6°C (for 4.9 hours) with filtrate from MST added showed no statistically discernible H_2 production above the background attributed to tramp organics in the caustic simulant. The HGR was approximately 2 x 10^{-7} (ft^3/h)/gal. Testing with MST filtrate was discontinued.
- Tests at 94°C ± 3°C (for 6.2 days) with 247 mg/L TOC as MCU solvent in the Tank 50 simulant showed no statistically discernible H_2 production above the background attributed to tramp organics in the caustic. The HGR was approximately 3 x 10^{-8} (ft^3/h)/gal. Testing with MCU solvent was discontinued.
- Tests with either grout-premix or BFS added to the Tank 50 simulant indicated H_2 production more than that attributed to the tramp organics in the caustic simulant. Testing of these additives continued with radioactive waste samples.

The final phase of the tests examined radioactive Tank 50 samples with either grout-premix or BFS added.

- The difference in the rate of production of H_2 for an overlaying air or nitrogen atmosphere appears insignificant
- Presence of BFS and grout-premix increases the HGR with a maximum measured rate of approximately 1.0 x 10^{-6} (ft^3/h)/gal at ~115°C. The difference between BFS and grout-premix was not significantly different within a 95% confidence level.
- Assuming a first order Arrhenius dependency, testing provides an average activation energy of 82.6 ± 9 kJ/mol for all the Tank 50 samples, as well as for Tank 50 samples with added grout-premix or BFS. However, when excluding room-temperature, 32°C, test results to consider the primarily effect of thermolysis, then the average activation energy similar 83.1 ± 12 kJ/mol, but containing slightly more

uncertainty. This value is comparable to that derived for thermolysis of organic constituents in Hanford Site waste.

- The experimental HGR results are bounded by calculated values based on the Hu equation adjusted to 25°C, following the literature protocol and the characterization data for the Tank 50 samples.

- Testing of Tank 50 samples at 32°C (for 26 days) showed an average HGR of 1.32 x 10^{-9} (ft^3/h)/gal ± 0.14 x 10^{-9}. This result is same order of magnitude to the Monte Carlo n-Particle Code estimate of radiolytic rate of 5.1 x 10^{-10} (ft^3/h)/gal from a 180-mL batch of waste. Furthermore, the result is conservatively bounded by the estimated SRR WCS radiolytic value for supernatant of 3.09 x 10^{-9} (ft^3/h)/gal and 5.08 x 10^{-9} (ft^3/h)/gal for slurry.

- Gas analyses from tests with Tank 50 (with and without added BFS or grout-premix) at 115°C showed ultra-trace quantities of an unidentified species. This temperature exceeds the operating limits for either Tank 50 or for SPF and the SDUs. Additional experimental work would be needed to identify the species.

- Longer testing periods give more accurate results, but the effect appears to reach an asymptote after 6 days.

- Simulant and radioactive results are in good agreement.

Note that during radioactive testing some of the reactors showed a small amount of leaking, which was not evident during shakedown or simulant testing. It is assumed from many operations of heating and cooling one or some of the many reactor seals became loose. In most cases the pressure drop during the heating periods was a fraction of a psi, from the starting pressure of ~20 psig. The worst case was from reactor HGV-2 during Test 5 when this reactor dropped 2.7 psi over the 17 hours at the target temperature. However, Test 5 had the lowest target temperature, i.e., 50°C, among the series of tests that had durations of ~16 hours, i.e., Tests 1-5. This lower temperature was expected to produce the lowest amount of H_2, which mitigate the effect of a leak. If a worst-case scenario is considered, e.g., 120°C for Tests 1 or 2, and considering a drop in pressure over 16 hours of 3 psi, then the error in the HGR result would be on the order of 8%. This assumes that the gas mixture is uniformly mixed so that a reactor leaked a uniform mixture of head-space gas. This is considered a good assumption because when sampling is performed generally 7 samples are taken at successively lower pressures from about 20 psig down to about 5 psig. The seven repeated measurements of ppm of H_2 from each reactor were the same, within measurement uncertainty. That is, mass is lost but he ratio of the number of parts of H_2 to the total number parts of gas molecules in the head space remains the same as each sample removes some the head-space gas. Future testing will change the seals more often.

6.0 Recommendations

Additional testing is warranted to understand the contribution of BFS and grout-premix to thermolytic H_2 generation at conditions more applicable to SPF and SDF. These tests added limiting amounts of the solids to the Tank 50 samples. Interpreting the implications for SPF and SDF requires experiments that examine prototypical process concentrations and that examine the full curing cycle. A risk exists that higher concentrations of the additives will results in higher peak HGRs than indicated by the tests documented within this study.

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Appendix A: Sealed Reactor Volumes, Liquid Additions, and Spike Additions

The appendix contains three tables. The first, Table 12, is the internal volumes of each reactor obtained from calibration [7.27; L0833-00239-05], before testing began, and note that these volumes are for empty reactors without the magnetic stirrer. The volume of the stirrer in each reactor is 2.715 mL and is considered when HGR is calculated because it reduces the head space volume the stirrer volume. The second, Table 13, is the liquid/gas volumes used during simulant tests along with the mass of spike material used. The last, Table 14, is the liquid/gas volumes used during the radioactive waste tests along with the mass of spike material used.

Table 12. Calibrated reactor volumes

Internal Volumes	
HGV No.	**Vol. (mL)**
2	**195.51**
3	**196.14**
4	**194.85**
5	**194.78**
6	**196.30**
7	**192.01**
8	**194.96**

Table 13. Fill volumes used for <u>simulant tests</u> along with gas used and spikes added

	Reactor Vessel Number HGV	Reactor Calibrated Volume mL	Reactor Head Space mL	Introduce Liquid Volume mL	Reactor Temp. at Fill °C	Liquid Simulant Density g/mL	Liquid Mass Needed g	Liquid Mass Used g	Reactor Temp. at Start °C	Liquid Simulant Density g/mL	Liquid Volume at Start mL	Actual Head Space mL	Adding 1 ml for GC tube mL (1)	Gas In Head Space	Type Spike in Simulant	Mass Spike in Simulant
Test 1-1 (4 hours)	2	195.51	100	95.51	21	1.228	**117.31**	118.00	23	1.228	96.07	99.44	100.44	N$_2$	None	NA
	3	196.14	100	96.14	21	1.228	**118.08**	118.25	23	1.228	96.27	99.86	100.86	N$_2$	None	NA
	4	194.85	100	94.85	21	1.228	**116.50**	117.30	23	1.228	95.50	99.35	100.35	N$_2$	None	NA
	5	194.78	100	94.78	21	1.228	**116.42**	117.60	23	1.228	95.74	99.04	100.04	N$_2$	None	NA
	6	196.30	100	96.30	21	1.228	**118.29**	118.38	23	1.228	96.37	99.93	100.93	N$_2$	None	NA
	7	192.01	20	172.01	21	1.228	**211.28**	213.93	22	1.228	174.17	17.84	18.84	N$_2$	None	NA
	8	194.96	20	174.96	21	1.228	**214.90**	215.21	21	1.228	175.21	19.75	20.75	N$_2$	None	NA
Test 1-1 (6 days)	7	192.01	20	172.01	21	1.228	**211.28**	213.93	22	1.228	174.17	17.84	18.84	Air-No H$_2$	None	NA
	8	194.96	20	174.96	21	1.228	**214.90**	215.21	21	1.228	175.21	19.75	20.75	Air-No H$_2$	None	NA
Test 1-2 (4 hours)	2	195.51	100	95.51	21	1.227	**117.21**	117.07	25	1.227	95.40	100.11	101.11	Air-No H$_2$	None	NA
	3	196.14	100	96.14	21	1.227	**117.98**	118.34	25	1.227	96.43	99.70	100.70	Air-No H$_2$	None	NA
	4	194.85	100	94.85	21	1.227	**116.40**	116.07	25	1.227	94.58	100.27	101.27	Air-No H$_2$	None	NA
	5	194.78	100	94.78	21	1.227	**116.31**	116.07	25	1.227	94.58	100.20	101.20	Air-No H$_2$	None	NA
	6	196.30	100	96.30	21	1.227	**118.18**	117.82	25	1.227	96.01	100.29	101.29	Air-No H$_2$	None	NA
Test 2 (4 hours)	2	195.51	100	95.51	19	1.23	**117.48**	117.58	21	1.23	95.59	99.92	100.92	N$_2$	Formate	0.135 g (2)
	3	196.14	100	96.14	19	1.23	**118.25**	118.22	21	1.23	96.11	100.02	101.02	N$_2$	Formate	0.136 g (2)
	4	194.85	100	94.85	19	1.23	**116.67**	116.01	21	1.23	94.32	100.53	101.53	Air-No H$_2$	Formate	0.133 g (2)
	5	194.78	100	94.78	19	1.23	**116.58**	116.60	21	1.23	94.80	99.98	100.98	Air-No H$_2$	Formate	0.134 g (2)
	6	196.30	100	96.30	19	1.23	**118.45**	118.07	21	1.23	95.99	100.31	101.31	Air-No H$_2$	None	Control
Test 3 (4 hours)	2	195.51	100	95.51	19	1.23	**117.48**	117.17	21	1.23	95.25797	100.25	101.25	Air-No H$_2$	Grout	0.228 g
	3	196.14	100	96.14	19	1.23	**118.25**	118.23	21	1.23	96.11959	100.02	101.02	Air-No H$_2$	Grout	0.223 g
	4	194.85	100	94.85	19	1.23	**116.67**	116.03	21	1.23	94.33537	100.51	101.51	Air-No H$_2$	G+Admix	0.222 g (3)
	5	194.78	100	94.78	19	1.23	**116.58**	116.35	21	1.23	94.59049	100.19	101.19	Air-No H$_2$	G+Admix	0.222 g (3)
	6	196.30	100	96.30	19	1.23	**118.45**	118.29	21	1.23	96.17163	100.13	101.13	Air-No H$_2$	MCU	(4)
	7	192.01	100	92.01	19	1.23	**113.17**	113.00	21	1.23	91.8726	100.14	101.14	Air-No H$_2$	MCU	(4)
	8	194.96	100	94.96	19	1.23	**116.80**	116.50	21	1.23	94.71577	100.24	101.24	Air-No H$_2$	None	Control
Test 4 (4 hours)	2	195.51	100	95.51	21	1.23	**116.96**	116.44	23	1.23	95.08	100.42	101.42	N$_2$	BFS	0.101 g
	3	196.14	100	96.14	21	1.23	**117.73**	116.95	23	1.23	95.50	100.63	101.63	N$_2$	BFS	0.101 g
	4	194.85	100	94.85	21	1.23	**116.15**	116.23	23	1.23	94.91	99.94	100.94	Air-No H$_2$	BFS	0.101 g
	5	194.78	100	94.78	21	1.23	**116.06**	116.22	23	1.23	94.90	99.87	100.87	Air-No H$_2$	BFS	0.101 g
	6	196.30	100	96.30	21	1.23	**117.93**	117.74	23	1.23	96.15	100.16	101.16	Air-No H$_2$	None	Control
	7	192.01	100	92.01	21	1.23	**112.68**	112.67	23	1.23	92.01	100.01	101.01	Air-No H$_2$	MST	0.252 g
	8	194.96	100	94.96	21	1.23	**116.28**	116.36	23	1.23	95.02	99.94	100.94	Air-No H$_2$	MST	0.256 g
Test 5 (6 days)	2	195.51	100	95.51	19	1.23	**117.48**	123.88	21	1.23	100.71	94.80	95.80	Air-No H$_2$	Grout	0.222 g
	3	196.14	100	96.14	19	1.23	**118.25**	119.15	21	1.23	96.87	99.26	100.26	Air-No H$_2$	Grout	0.222 g
	4	194.85	100	94.85	19	1.23	**116.67**	116.00	21	1.23	94.31	100.54	101.54	Air-No H$_2$	Formate	0.133 g (2)
	5	194.78	100	94.78	19	1.23	**116.58**	117.28	21	1.23	95.35	99.43	100.43	Air-No H$_2$	Formate	0.135 g (2)
	6	196.30	100	96.30	19	1.23	**118.45**	118.31	21	1.23	96.19	100.11	101.11	Air-No H$_2$	None	Control
	7	192.01	100	92.01	19	1.23	**113.17**	113.19	21	1.23	92.02	99.99	100.99	Air-No H$_2$	MCU	(4)
	8	194.96	100	94.96	19	1.23	**116.80**	119.83	21	1.23	97.42	97.53	98.53	Air-No H$_2$	MCU	(4)

(1) When calculating the HGR these head volumes are by reduced by 2.715 mL due to the volume of the stirrer bar.

(2) For the formate spike a separate simulant was made that had 1.4124 g/L of sodium formate, which is expected to be 0.247 g/L for TOC.

(3) Planned addition of Admix (Daratard 17) was 0.00075 g/gGrout or 0.00017 g per reactor (the minimum that could be injection was between 0.004 g and 0.006 g)

(4) Planned addition of MCU Solvent (75 wt% Isopar) 15 ppm, equilavent to 0.0018 g per 100 mL simulant (minimum possible was between 0.004 g and 0.006 g)

Table 14. Fill volumes used for Tank 50 tests along with gas used and spikes added

	Reactor Vessel Number HGV	Reactor Calibrated Volume mL	Reactor Head Space mL	Introduce Liquid Volume mL	Reactor Temp. at Fill °C	Liquid Simulant Density g/mL	Liquid Mass Needed g	Liquid Mass Used g	Reactor Temp. at Start °C	Liquid Simulant Density g/mL	Liquid Volume at Start mL	Actual Head Space mL	Adding 1 ml for GC tube mL (1)	Gas In Head Space	Type Spike in Waste	Mass Spike in Waste
Test 1 (16 hours)	2	195.51	100	95.51	19	1.237	**118.14**	118.05	21.00	1.237	95.43	100.08	101.08	N₂	None	Control
	3	196.14	100	96.14	19	1.237	**118.92**	118.18	21.00	1.237	95.54	100.60	101.60	N₂	BFS	0.116 g
	4	194.85	100	94.85	19	1.237	**117.33**	115.31	21.00	1.237	93.22	101.63	102.63	N₂	Grout	0.230 g
Test 2 (16 hours)	2	195.51	100	95.51	19	1.237	**118.14**	118.32	22	1.237	95.65	99.86	100.86	Air-No H₂	None	Control
	3	196.14	100	96.14	19	1.237	**118.92**	118.93	22	1.237	96.14	99.99	100.99	Air-No H₂	BFS	0.107 g
	4	194.85	100	94.85	19	1.237	**117.33**	116.17	22	1.237	93.91	100.94	101.94	Air-No H₂	Grout	0.236 g
Test 3 (16 hours)	2	195.51	100	95.51	19	1.237	**118.14**	117.61	21	1.237	95.08	100.43	101.43	Air-No H₂	None	Control
	3	196.14	100	96.14	19	1.237	**118.92**	118.37	21	1.237	95.69	100.44	101.44	Air-No H₂	BFS	0.103 g
	4	194.85	100	94.85	19	1.237	**117.33**	116.78	21	1.237	94.41	100.44	101.44	Air-No H₂	Grout	0.225 g
Test 4 (16 hours)	2	195.51	100	95.51	19	1.237	**118.14**	117.95	21	1.237	95.35	100.16	101.16	Air-No H₂	None	Control
	3	196.14	100	96.14	19	1.237	**118.92**	118.78	21	1.237	96.02	100.12	101.12	Air-No H₂	BFS	0.102 g
	4	194.85	100	94.85	19	1.237	**117.33**	116.58	21	1.237	94.25	100.60	101.60	Air-No H₂	Grout	0.227 g
Test 5 (16 hours)	2	195.51	100	95.51	23	1.237	**118.14**	118.09	23	1.237	95.47	100.04	101.04	Air-No H₂	None	Control
	3	196.14	100	96.14	23	1.237	**118.92**	118.39	23	1.237	95.70	100.43	101.43	Air-No H₂	BFS	0.103 g
	4	194.85	100	94.85	23	1.237	**117.33**	116.06	23	1.237	93.82	101.03	102.03	Air-No H₂	Grout	0.228 g
Test 6 (26 days)	5	194.78	20	174.78	19	1.237	**216.20**	215.85	22	1.237	174.49	20.28	21.28	Air-No H₂	None	NA
	6	196.30	20	176.30	19	1.237	**218.09**	216.95	22	1.237	175.38	20.92	21.92	Air-No H₂	None	NA
Test 7 (6 days)	2	195.51	100	95.51	19	1.237	**118.14**	116.90	21	1.237	94.50	101.00	102.00	Air-No H₂	BFS	0.101 g
	3	196.14	100	96.14	19	1.237	**118.92**	118.34	21	1.237	95.67	100.47	101.47	Air-No H₂	Grout	0.225 g
	4	194.85	100	94.85	19	1.237	**117.33**	117.09	21	1.237	94.66	100.19	101.19	Air-No H₂	None	Control
	5	194.78	100	94.78	19	1.237	**117.24**	117.63	21	1.237	95.09	99.69	100.69	Air-No H₂	BFS	0.101 g
	6	196.30	100	96.30	19	1.237	**119.13**	118.69	21	1.237	95.95	100.35	101.35	Air-No H₂	Grout	0.220 g

(1) When calculating the HGR these head volumes are by reduced by 2.715 mL due to the volume of the stirrer bar.

Appendix B: Instrument List

Measurement and Testing Equipment List

Table 15 lists all the instruments connected to the DAS that could be electronically recorded during a test.

Table 15. Measurement and test equipment connected to the DAS

DAS INSTRUMENTS								
DAS Ch. Number	M&TE Number TR-	Instrument Name	MFG	Model	Calibrated Range	Tolerance	Calibration Date	Pre Test Uncertainty
0	TR-40326	T0	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.15 °C
1	TR-40332	T1	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.99 °C
2	TR-40319	T2	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.38 °C
3	TR-40333	T3	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.95 °C
4	TR-40324 (1)	T4	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.51 °C
5	TR-40320	T5	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.13 °C
6	TR-40331	T6	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.08 °C
7	TR-40343	T7	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.85 °C
8	TR-40325	T8	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.14 °C
9	TR-40321	T9	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.08 °C
10	TR-40326	T10	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.15 °C
11	TR-40328	T11	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/-1.15 °C
12	TR-40330	T12	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.19 °C
13	TR-40323	T13	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.32 °C
14	TR-40317	T14	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.84 °C
15	TR-40318	T15	Omega	HKQSS-116U-12	0-200°C	+/-2.2°C	Before and After	+/- 1.39 °C
16	TR-40334	P0	Setra	225G-150P-G-D4-11-06	0-150 PSIG	+/-0.75 PSIG	8/24/2018	+/- 0.218 psig
17	TR-40335	P1	Setra	225G-150P-G-D4-11-06	0-150 PSIG	+/-0.75 PSIG	8/25/2018	+/- 0.300 psig
18	TR-40341	P2	Setra	225G-150P-G-D4-11-06	0-150 PSIG	+/-0.75 PSIG	8/26/2018	+/- 0.224 psig
19	TR-40337	P3	Setra	225G-150P-G-D4-11-06	0-150 PSIG	+/-0.75 PSIG	8/27/2018	+/- 0.316 psig
20	TR-40338	P4	Setra	225G-150P-G-D4-11-06	0-150 PSIG	+/-0.75 PSIG	8/28/2018	+/- 0.300 psig
21	TR-40339	P5	Setra	225G-150P-G-D4-11-06	0-150 PSIG	+/-0.75 PSIG	8/29/2018	+/- 0.287 psig
22	TR-40340	P6	Setra	225G-150P-G-D4-11-06	0-150 PSIG	+/-0.75 PSIG	8/30/2018	+/- 0.272 psig
23	TR-40315 (3)	MF1	Omega	FMA-4303	0-10 SCCM	+/-1% F.S.	7/28/2018	

Notes:

(1) During simulant Test 1 on 1 Nov. 2017 TC T4 failed, so spare TC T14 replaced it.
    However, the DAS channel and TC extension cord are those originally used for TC T4.

(2) During radioactive Test 6, HGV-5 & HGV-6 were used for a 26-day test that occurred
    simultaneously with heated Tests 1 through 5 and heated to a much lower
    temperature. Therefore, they were located on the individual hotplates that
    were used the by HGV-7 and HGV-8 during simulant testing. Therefore, HGV-5
    used DAS channel 10 & T10 and HGV-6 used DAS channel 12 & T12 for this single
    test. However, those reactors continued to used their original TC and pressure
    transducer, i.e., T7 & P3 (HGV-5) and T9 & P4 (HGV-6).

(3) The flowrate of this meter was found to be too low for the test therefore, it
    was never used, but it is included on the DAS.

(4) During the water calibration check using HGV-4, the internal temperature was
    measured by a separate TC (M&TE No. TR-40345).

Table 16 lists all the instruments not connected to the DAS and were recorded manually, or were used only for monitoring purposes. These include the mass balances, temperature controllers, gas flowmeters, and hot plates.

Table 16. Measurement and test equipment not connected to the DAS

Non-DAS Equipment-Aiken County Technical Laboratory						
Equipment Name	Description	MFG	Model	Calibration Expiration Date	Range	Tolerance
Stirrer	9 Place Stirrer	Cole Parmer	EW-51450-73	N/A	N/A	N/A
Temperature Controller	TMP CNTRLR	Omega	MCS-2110K-R	N/A		N/A
Temperature Controller	TMP CNTRLR	Omega	MCS-2110K-R	N/A		N/A
Temperature Controller	TMP CNTRLR	Omega	MCS-2110K-R	N/A		N/A
GT3-T005	Temperature Indicator	Digi-Sense	92000-00	N/A	0-1000°C	+/-0.1% RDG & +/- 2°C
TR-40150	3 Place Balance	Mettler-Toledo	AB-304-S	2/18/2019	0-320 g	+/- 0.4% RDG
TR-03930	Thermistor	Digi-Sense	ThermoLogR	2/21/2018	-40 - 125°C	+/-0.2°C
FM1K-11	Mass Flowmeter	MKS	179A13CS3BM	10/18/2018	0-1000 SCCM	2% of RDG
AD-0096	3 Place Balance	Mettler-Toledo	B026046413	10/24/2019	0-320 g	+/-0.003 g
Hot Plate	Hot Plate/Stirrer	Torrey Pines Scientific	HS40	N/A	N/A	N/A
Hot Plate	Hot Plate/Stirrer	Torrey Pines Scientific	HS40	N/A	N/A	N/A
Non-DAS Equipment used in 773-A, C-162						
Equipment Name	Description	MFG	Model	Calibration Expiration Date	Range	Tolerance
Overtemperature Controller	Independent OT CNTR	Glas-Col	OTP-1800			
GT1-880	4 Place Balance	Mettler	AG285	8/29/2018	0-210 g	+/-0.04 g
Temperature Controller	TMP CNTRLR	Omega	MCS-2110K-R	N/A		N/A
Temperature Controller	TMP CNTRLR	Omega	MCS-2110K-R	N/A		N/A
TR-40351	Rotameter	Brooks	1355EHA8CFA1A	1/16/2020	51.8 - 517.8 cc/min air	+/- 25 cc/min
Hot Plate	Hot Plate/Stirrer	Torrey Pines Scientific	HS40	N/A	N/A	N/A
Hot Plate	Hot Plate/Stirrer	Torrey Pines Scientific	HS40	N/A	N/A	N/A
GT3-T005	Temperature Indicator	Digi-Sense	92000-00	N/A	0-1000°C	+/-0.1% RDG & +/- 2°C

Appendix C: DAS Channel Assignments and Calibrations

Table 17 lists the DAS channels assigned to the instrument employed, Table 18 the channel calibration data for seven pressure transducers and one mass flow meter, and finally Table 19 shows the transfer equations, which were obtained using calibration data and range of instrument for pressure transducers shown in Table 16.

Table 17. DAS Channel assignments, instrument names, and M&TE numbers

DAS Setup for PISA Sealed Reactor System			
Assigned Measurement	DAS Channel	Instrument Name	M&TE Number
HGV-2 Body Temperature	0	T0	TR-40326
HGV-2 Pressure Transducer Temperature	1	T1	TR-40332
HGV-3 Body Temperature	2	T2	TR-40319
HGV-3 Pressure Transducer Temperature	3	T3	TR-40333
HGV-4 Body Temperature	4	T4 (1) (4)	TR-40324
HGV-4 Pressure Transducer Temperature	5	T5	TR-40320
HGV-5 Body Temperature	6	T6	TR-40331
HGV-5 Pressure Transducer Temperature	7	T7	TR-40343
HGV-6 Body Temperature	8	T8	TR-40325
HGV-6 Pressure Transducer Temperature	9	T9	TR-40321
HGV-7 Body Temperature	10	T10 (2)	TR-40326
HGV-7 Pressure Transducer Temperature	11	T11	TR-40328
HGV-8 Body Temperature	12	T12 (2)	TR-40330
HGV-8 Pressure Transducer Temperature	13	T13	TR-40323
Spare Temperature: Ambient or reactor	14	T14 (1)	TR-40317
Spare Temperature: Ambient or reactor	15	T15	TR-40318
HGV-2 Pressure Transducer Pressure	16	P0	TR-40334
HGV-3 Pressure Transducer Pressure	17	P1	TR-40335
HGV-4 Pressure Transducer Pressure	18	P2 (2)	TR-40341
HGV-5 Pressure Transducer Pressure	19	P3 (2)	TR-40337
HGV-6 Pressure Transducer Pressure	20	P4 (2)	TR-40338
HGV-7 Pressure Transducer Pressure	21	P5	TR-40339
HGV-8 Pressure Transducer Pressure	22	P6	TR-40340
Mass Flow Meter 0 to 10 ml/minute	23	MFI (3)	TR-40315

Notes:
(1) During simulant Test 1 on 1 Nov. 2017 TC T4 failed, so spare TC T14 replaced it. However, the DAS channel and TC extension cord are those originally used for TC T4.
(2) During radioactive Test 6, HGV-5 & HGV-6 were used for a 26-day test that occurred simultaneously with heated Tests 1 through 5 and heated to a much lower temperature. Therefore, they were located on the individual stirrer/hotplates that were used the by HGV-7 and HGV-8 during simulant testing. Therefore, HGV-5 used DAS channel 10 & T10 and HGV-6 used DAS channel 12 & T12 for this single test. However, those reactors continued to use their original TC and pressure transducer, i.e., T7 & P3 (HGV-5) and T9 & P4 (HGV-6).
(3) The flowrate of this meter was found to be too low for the test therefore, it was never used, but it is included on the DAS.
(4) During the water calibration check using HGV-4, the internal temperature was measured be a separate TC (M&TE No. TR-40345).

Table 18. Channel calibration data for seven pressure transducers and one mass flow meter

DAS Cal and Equations

Chan 16 (P0)			Chan 17 (P1)			Chan 18 (P2)			Chan 19 (P3)			Chan 20 (P4)		
Nom		Out	Nom		Out	Nom		Out	Nom		Out	Nom		Out
(mA)	(mA)	(V)	(mA)	(mA)	(V)	(mA)	(mA)	(V)	(mA)	(mA)	(V)	(mA)	(mA)	(V)
4	4.00	2.02	4	4.00	1.99	4	4.00	2.00	4	4.00	1.99	4	4.00	2.00
8	8.00	4.04	8	8.00	3.98	8	8.00	3.99	8	8.00	3.99	8	8.00	4.00
12	12.00	6.04	12	12.00	5.98	12	12.00	5.98	12	12.00	5.98	12	12.00	6.00
16	16.00	8.05	16	16.00	7.97	16	16.00	7.98	16	16.00	7.97	16	16.00	8.00
20	20.00	10.07	20	20.00	9.96	20	20.00	9.97	20	20.00	9.97	20	20.00	10.00
In = m*Out + b			In = m*Out + b			In = m*Out + b			In = m*Out + b			In = m*Out + b		
(mA = m*VDC + b)			(mA = m*VDC + b)			(mA = m*VDC + b)			(mA = m*VDC + b)			(mA = m*VDC + b)		
m=	1.989		m=	2.008		m=	2.008		m=	2.007		m=	2.001	
b=	-0.017		b=	-0.001		b=	-0.008		b=	0.002		b=	-0.005	
TR-40334			TR-40335			TR-40341			TR-40337			TR-40338		
psig = m*mADC + b			psig = m*mADC + b			psig = m*mADC + b			psig = m*mADC + b			psig = m*mADC + b		
m=	9.377		m=	9.389		m=	9.387		m=	9.387		m=	9.252	
b=	-36.898		b=	-37.312		b=	-37.218		b=	-37.406		b=	-36.262	
Combined			Combined			Combined			Combined			Combined		
psig = m*VDC + b			psig = m*VDC + b			psig = m*VDC + b			psig = m*VDC + b			psig = m*VDC + b		
m=	18.646		m=	18.850		m=	18.844		m=	18.835		m=	18.517	
b=	-37.062		b=	-37.318		b=	-37.292		b=	-37.388		b=	-36.310	

Chan 21 (P5)			Chan 22 (P6)			Chan 23 (MFM1)		
Nom		Out	Nom		Out	Nom		Out
(mA)	(mA)	(V)	(mA)	(mA)	(V)	VDC	VDC	(V)
4	4	1.994	4	4	2.0045	0	0	0
8	8	3.9955	8	8	4.004	1	1	1
12	12	5.9875	12	12	6.005	2	2	2
16	16	7.986	16	16	8.004	3	3	3
20	20	9.981	20	20	10.0065	4	4	4
						5	5	5
In = m*Out + b			In = m*Out + b			In = m*Out + b		
(mA = m*VDC + b)			(mA = m*VDC + b)			(mA = m*VDC + b)		
m=	2.00355549		m=	1.99959995		m=	1	
b=	0.00110686		b=	-0.0071978		b=	0	
TR-40339			TR-40340					
psig = m*mADC + b			psig = m*mADC + b			mL/min = m*VDC + b		
m=	9.40048523		m=	9.32035152		m=	2.082	
b=	-37.405076		b=	-36.844022		b=	-0.033	
Combined			Combined			Combined		
psig = m*VDC + b			psig = m*VDC + b			smL/min = m*VDC + b		
m=	18.8343938		m=	18.6369744		m=	2.082	
b=	-37.394671		b=	-36.911108		b=	-0.033	

Table 19. Transfer equations for the seven pressure transducers

Ch			mADC		+b		PSIG=*mVDC	+b
16	TR-40334	PSIG=	9.376667	*mA	-36.8983		18.646	-37.062
17	TR-40335	PSIG=	9.388899	*mA	-37.3122		18.850	-37.318
18	TR-40341	PSIG=	9.386558	*mA	-37.2178		18.844	-37.292
19	TR-40337	PSIG=	9.386651	*mA	-37.4064		18.835	-37.388
20	TR-40338	PSIG=	9.251581	*mA	-36.2623		18.517	-36.310
21	TR-40339	PSIG=	9.400485	*mA	-37.4051		18.834	-37.395
22	TR-40340	PSIG=	9.320352	*mA	-36.844		18.637	-36.911

Appendix D: Simulant Make-up Direction

Example R&D Direction of Tank 50 Simulant Preparation

Date: October 23rd, 2017
PIs: C.A. Nash, A.M. Howe
Managers: B.J. Wiedenman, G.A. Morgan

Applicable Reference Documents:
HAP SRNL-L3100-2008-00081, Rev. 6
HAP SRNL-L3100-2017-00079, Rev. 0

Note: These instructions are for the development of a batch size, 1.0 L Tank 50 Simulant to evaluate and conduct analyses.

Hazards (unique activity-specific hazards):
Chemical hazard for caustic simulant (pH >14): contact with chemicals, splashing, and spills
Potential hot surfaces
Potential heat produced from exothermic reactions

Hazard Controls (activity-specific hazards controls for above hazards):
The simulant preparation will be completed in a chemical hood to protect the workers.
Personnel involved will wear appropriate PPE: lab coat, 5 mil nitrile gloves, and safety glasses.
Leather or other protective gloves when manipulating glassware or handling hot equipment and samples

In the event of a major spill outside of the hood, follow SWIMS:
Stop Work
Warn others
Isolate spill only if safe to do so
Minimize the hazard exposure by leaving lab
Secure the area so others cannot enter lab
Contact your supervisor and IH

In the event of skin exposure or contact, remove PPE and flush for minimum of 15 minutes and then report to Medical (ambulance/hospital).

M&TE / MS&E (if not on list, record in notes)

Description	M&TE / MS&E #	Expiration Date
Balance		
Temperature		

Preparation of Tank 50 Simulant for Evaluation and Analysis

Set up a magnetic stir plate in a chemical fume hood, with a clean 1.00 L volumetric flask. Make a note of flask uncertainty at temperature if printed on flask.

Label the flask "Tank 50 Simulant". Also add to the label the owner, date, and hazard "corrosive".

Weigh the empty flask with cap: _____ g

Insert stir bar using an external magnet to prevent damage to the flask.

Retrieve NaOH pellets (not solution; pellets appear to be relatively free of organic contamination) and the chemicals listed in Table 1. Ensure chemicals have not degraded due to age or past the recommended shelf life.

Measure 550 mL ± 10 mL high purity (HPLC grade) water.

Check the assay of the NaOH pellets (see bottle label). Adjust the amount to add per the assay (for example, 98% assay needs 102/0.98 = 104.1 grams). Slowly add 102.000 g + assay adjustment of the NaOH pellets. Actual mass added: _____ g. Dissolution creates sensible heat but will not boil the solution.

Commence mixing and weigh the chemicals in Table 1 below and separately add to flask (use weigh boat to avoid overshooting the targets). No assay adjustment is needed for these. Separately add the chemicals in the order listed in the Table 1 below and record the actual mass added. Use a small amount of high purity (HPLC grade) water to rinse the weigh boat, if necessary to transfer the entire quantity into the flask. Ensure that each component is fully dissolved before adding additional species. If component does not fully dissolve, slightly warm the solution and continue stirring.

Table 1.

Chemical Name	Formula	Target Mass (g)	Actual Mass (g)
Aluminum Nitrate Nonahydrate	$Al(NO_3)_3 \cdot 9H_2O$	56.270 Add slowly (5 - 10 g at a time)*	
Sodium Carbonate	Na_2CO_3	28.620	
Sodium Sulfate	Na_2SO_4	7.386	
Sodium Nitrate	$NaNO_3$	118.150	
Sodium Nitrite	$NaNO_2$	42.780	

* Aluminum nitrate should be added slowly in 5 to 10 g portions with vigorous mixing. White solids should not be forming during this step.

Continue mixing until all chemicals dissolve in the flask (approximately 1 hour)

If solids do not dissolve contact PI.

After all chemicals have dissolved, adjust level to the 1.00 L mark with high purity (HPLC grade) water. Stir for half an hour with the magnetic stir bar that is in the flask.

Remove the magnetic stir bar using an external magnet and allow the solution to cool below 30°C if it is not below that temperature. The liquid level will be slightly below the 1.00-liter mark because of stir bar removal, solution contraction, and cooling.

Adjust the level to the 1.00 L mark with high purity (HPLC grade) water. Cap and gently agitate the flask as needed so that this small portion of water is mixed into the batch of simulant.

Measure the temperature of the prepared solution: _____ °C

Weight the full 1.00 L volumetric flask with cap.

      Full 1.00 L volumetric flask + cap weight: _____ g

Let the Simulant settle in the volumetric flask overnight.

Label the bottom of a 0.2μm 1.0L Filter System "Tank 50 Simulant". Also add to the label the owner, date, and hazard "corrosive".

Weigh the empty 1.0L filter bottle with cap: _____ g

Filter the simulant.

Weigh the full 1.00 L filter bottle with cap.

Full 1.00 L filter bottle + cap weight: _____ g

Obtain two 10 mL samples of simulant and submit to PSAL for ICP-ES suites, IC Anions Label as "PSAL - Tank 50 Simulant A" and "PSAL – Tank 50 Simulant B". Also add to the labels the owner, date, and hazard "corrosive". Obtain PSAL numbers from PI.

Ensure that work area and equipment is properly cleaned. Properly return and store equipment and chemicals.

NOTES:

Appendix E: Radioactive Tank 50 Waste Used for Sealed Reactor Tests

The sample used for sealed system thermolysis testing is the variable depth sample taken from Tank 50. The sample was obtained ~ 66" from the tank bottom after the tank had been agitated for ~ 4.4 hours using a single pump on Wednesday, October 18, 2017. The sample identification is HTF-50-17-99. Chemical species are shown in Table 20 and radionuclides are shown in Table 21. The concentrations presented in the tables (except upper limits) are averages based on triplicate analyses. The standard deviation of each average is also presented. Several of the contaminants were either not detected in the slurry samples or detected at values below the method reporting limit (MRL). For contaminants not detected or detected below the MRL, the result is preceded by a "<", which indicates the result is an upper limit based on the sensitivity of the method used to analyze the individual analyte. Data reported for atomic absorption (AA), cold-vapor atomic absorption (CVAA), inductively coupled plasma atomic emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS) are derived from the digested Tank 50 supernatant by the aqua regia method. Values are also provided for: Ion Chromatography (IC), Volatile Organic Analysis (VOA), Semi-Volatile Organic Analysis (SVOA), Total Inorganic Carbon (TIC), TOC, and Total Base.

Table 20. Chemical analytes from Tank 50 solution analysis

Chemical Name (Formula)	Method	Average Concentration (mg/L)	Std. Dev.
Aluminum (Al)	ICP-ES	5.04E+03	1.26E+02
Carbonate (CO_3^{2-})	TIC	1.52E+04	5.00E+01
Chloride (Cl^-)	IC	5.14E+02	9.07E+00
Fluoride (F^-)	IC	<1.00E+02	NA
Free Hydroxide (OH^-)	Total Base	3.38E+04	1.70E+02
Nitrate (NO_3^-)	IC	1.27E+05	6.24E+03
Nitrite (NO_2^-)	IC	2.83E+04	1.23E+03
Oxalate ($C_2O_4^{2-}$)	IC	5.92E+02	2.29E+01
Phosphate (PO_4^{3-})	IC	3.29E+02	1.01E+01
Sulfate (SO_4^{2-})	IC	4.74E+03	1.72E+02
Formate (HCO_2^-)	IC	2.78E+02	5.69E+00
Arsenic (As)	ICPMS	<1.20E+00	NA
Boron (B)	ICP-ES	5.17E+01	2.11E+00
Barium (Ba)	ICP-ES	8.10E-01	4.68E-01
Beryllium (Be)	ICP-ES	1.05E-01	1.34E-02
Cadmium (Cd)	ICP-ES	< 2.86E+00	NA
Chromium (Cr)	ICP-ES	4.86E+01	1.73E+00
Cobalt (Co)	ICP-MS	<2.39E-02	NA
Copper (Cu)	ICP-ES	< 1.05E+01	NA
Iron (Fe)	ICP-ES	< 4.53E+00	NA
Lead (Pb)	ICP-MS	3.79E-01	1.19E-02
Lithium (Li)	ICP-ES	7.81E+00	6.88E-01
Manganese (Mn)	ICP-ES	3.34E+00	1.66E-01
Molybdenum (Mo)	ICP-ES	1.93E+01	1.03E+00
Sodium (Na)	ICP-ES	1.20E+05	6.13E+03
Sodium (Na)	ICP-ES	5.24 M	0.27
Nickel (Ni)	ICP-ES	< 4.90E+00	NA
Silicon (Si)	ICP-ES	<9.58E+00	NA
Strontium (Sr)	ICP-ES	< 2.03E-01	NA
Zinc (Zn)	ICP-ES	7.27E+00	2.30E-01
Total Mercury (Hg)	CVAA	5.89E+01	3.98E-01
Selenium (Se)	ICPMS	<1.20E+00	NA
Silver (Ag)	ICP-ES	< 2.92E+00	NA
Potassium (K)	ICP-ES	5.26E+02	2.30E+01
Butanol (C_4H_9OH)	VOA	< 5.00E-01 [c]	NA
Propanol (C_3H_7OH)	VOA	< 2.50E-01 [c]	NA
Phenol (C_6H_5OH)	SVOA	< 1.00E+01 [c]	NA
Benzene (C_6H_6)	VOA	< 1.50E-01 [b]	NA
Tributylphosphate[TBP] (($C_4H_9O)_3PO$)	SVOA	< 7.50E-01 [b]	NA
Toluene ($C_6H_5CH_3$)	VOA	< 1.50E-01 [b]	NA
Total Organic Carbon (----)	TOC	2.73E+02	3.06E+00
Density (slurry)	Measured (22.4ºC)	1.2371 g/mL	0.0001

Table 21. Radionuclide analytes from Tank 50 solution analysis

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.
Strontium-90 (^{90}Sr)	Sr-90 Liquid Scintillation	1.95E+04	1.33E+03
Technetium-99 (^{99}Tc)	Tc-99 Liquid Scintillation	4.37E+04	2.77E+03
Cesium-137 (^{137}Cs)	Gamma Scan	9.20E+05	9.38E+03
Uranium-233 (^{233}U)	ICP-MS	< 2.32E+02	NA
Uranium-235 (^{235}U)	ICP-MS	2.11E-01	4.93E-03
Total Alpha	Liquid Scintillation Counting (Cs removed)	2.61E+04	1.12E+03
Total Beta	Liquid Scintillation Counting	1.23E+06	2.60E+03
Total Gamma	Gamma Scan	8.72E+05	5.12E+03
Aluminum-26 (^{26}Al)	Gamma Scan (Cs removed)	1.50E-01	8.60E-03
Cobalt-60 (^{60}Co)	Gamma Scan (Cs removed)	3.64E-01	1.22E-01
Potassium-40 (^{40}K)	Gamma Scan (Cs removed)	< 2.05E+00	NA
Yttrium-90 (^{90}Y)	Secular Equilibrium w/ 100% of Sr-90	1.95E+04	1.33E+03
Zirconium-93 (^{93}Zr)	ICP-MS	< 1.20E+02	NA
Rhodium-106 (^{106}Rh)	Secular Equilibrium w/ 100% of Ru-106	< 1.51E+00	NA
Ruthenium-106 (^{106}Ru)	Gamma Scan (Cs removed)	< 1.51E+00	NA
Antimony-125 (^{125}Sb)	Gamma Scan (Cs removed)	1.04E+01	2.48E-01
Tellurium-125m (^{125m}Te)	Secular Equilibrium w/ 100% of Sb-125	1.04E+01	2.48E-01
Tin-126 (^{126}Sn)	Gamma Scan (Cs removed)	4.52E+02	3.26E+01
Cesium-134 (^{134}Cs)	Gamma Scan	< 7.57E+01	NA
Cesium-135 (^{135}Cs)	ICP-MS	9.35E+01	NA
Barium-137m (^{137m}Ba)	Calculation (Secular Equilibrium w/ 94.6% of Cs-137)	8.71E+05	8.87E+03
Cerium-144 (^{144}Ce)	Gamma Scan (Cs removed)	< 2.17E+00	NA
Europium-154 (^{154}Eu)	Gamma Scan (Cs removed)	1.28E+00	4.23E-01
Europium-155 (^{155}Eu)	Gamma Scan (Cs removed)	< 1.20E+00	NA
Radium-228 (^{228}Ra)	Gamma Scan (Cs removed)	< 8.96E-01	NA
Thorium-232 (^{232}Th)	ICP-MS	< 2.63E-03	NA
Uranium-234 (^{234}U)	ICP-MS	< 1.50E+02	NA
Uranium-236 (^{236}U)	ICP-MS	< 1.55E+00	NA
Uranium-238 (^{238}U)	ICP-MS	3.71E+00	3.85E-02
Neptunium-237 (^{237}Np)	ICP-MS	< 1.69E+01	NA
Plutonium-242 (^{242}Pu)	ICP-MS	< 9.14E+01	NA
Plutonium-244 (^{244}Pu)	ICP-MS	< 4.25E-01	NA
Americium-241 (^{241}Am)	Gamma Scan (Cs removed)	7.75E+00	1.27E-01

Appendix F: Shakedown Individual Test Results

Pre-Test Evaluation: Shakedown

Before any testing with either simulant or Tank 50 waste began the reactors were tested to determine if they were leak tight and impermeable to H_2. The Run plan [7.24,Table 2] included a series of shakedown tests, which are shown in Table 5. Note, the target temperatures in this, and all subsequent tables are the values listed in the approved Task Plan [7.24]; however, due to the internal temperature correction discussed in [2.4.1] the actual test temperatures are indicated directly on each graph

Table 5 (repeated). Shakedown tests to baseline sealed reactors

Test #	Test Type	Nominal (1) Temperature °C	Start Pressure, psig	Fill Gas	Liquid	Amount of liquid, mL	Duration h
1	Leak Tests	120	10 to 25	Air, No H_2	None	Zero	>4
2	Standard H2	25	10 to 25	10 ppm H_2	None	Zero	>4
3	1 M NaOH	50	10 to 25	N_2, No H_2	1 M NaOH	180	>4
4	Al pellet – 150 μg	50	10 to 25	N_2, No H_2	1 M NaOH	180	>4
5	1 M NaOH	120	10 to 25	N_2, No H_2	1 M NaOH	100	>4
6	Al pellet – 750 μg	120	10 to 25	N_2, No H_2	1 M NaOH	100	>4

Note (1): Nominal is ±5°C.

The data for each test will be presented by the, Temperature History, Pressure History, H_2 measured during the gas sampling of each reactor after it returned to room temperature, and, for tests that contain liquid, the HGR, which is adjusted to a pressure of 1 atmosphere (14.7 psia) and a temperature of 25°C. That is, for the HGR calculation, the sampling initial pressure, which was usually close to 20 psig, and temperature, which was usually between 22°C to 28°C, were adjusted so all the graphical data are adjusted to 1 atm and 25°C. The equation used for HGR was:

[[(Head Space Volume, ft^3) • A • H_2 Measured, ppm / 1000000] / (Test Time, hours)] / Volume Liquid, gal

Where A = [Pinitial sample / Pstandard] [Tstandard/Tsampling] =
[(Initial Sample Head Pressure, psig + 14.7 psia) / 14.7 psia] [298 K / (T°C at sampling+273 K)]

With Pstandard = 14.7 psia and Tstandard = 25°C

The following data for each test will be presented by the measurements of: Temperature History, Pressure History, and the H_2, which was obtained during the gas sampling of each reactor after it returned to room temperature. For tests where the reactors contain liquid, this information, along with reactor specifics, is used to create the last graph, which shows the result of a calculation of HGR. That calculation is adjusted to a pressure of 1 atmosphere (14.7 psia) and a temperature of 25°C. That is, for the HGR calculation, the sampling initial pressure, which was usually close to 20 psig, and temperature, which was usually between 22°C to 28°C, were adjusted so all the graphical data are adjusted to 1 atm and 25°C. The equation used for HGR was:

[[(Head Space Volume, ft^3) • A • H_2 Measured, ppm / 1000000] / (Test Time, hours)] / Volume Liquid, gal

Where A = [Pinitial sample / Pstandard] [Tstandard/Tsampling] =
[(Initial Sample Head Pressure, psig + 14.7 psia) / 14.7 psia] [298 K / (T°C at sampling+273 K)]

With Pstandard = 14.7 psia and Tstandard = 25°C

Test 1: Gas-only leak test at with air, no H₂

For this very first shakedown test the intent was to show the reactors were leak-tight and did not lose or gain H_2 through permeability. All seven reactors were completely empty and purged with 15+ reactor volumes of H_2-free air, heated to 120°C and held for approximately 4 hours. They contained no liquid. Heating was then stopped and the reactors were allowed to cool overnight to measurement any H_2 on the following day. Note, that the H_2-free gas was measured directly from the supply cylinder with the GC before the test and no H_2 was detected. Also note that for the GC used the LOD was 1 ppm, but H_2 had to be above 3 ppm to be quantifiable. Figure 22 shows that the reactors were held at an average of 114°C for over 4 hours. Figure 23 shows the increase in reactor pressure as the temperature increased. The pressures are different due to the initial pressure, which was close to 20 psig ± 5 psig. Figure 24 shows that either H_2 was not detected or below the quantifiable level; therefore, for this first test the reactors were considered leak-tight and impermeable.
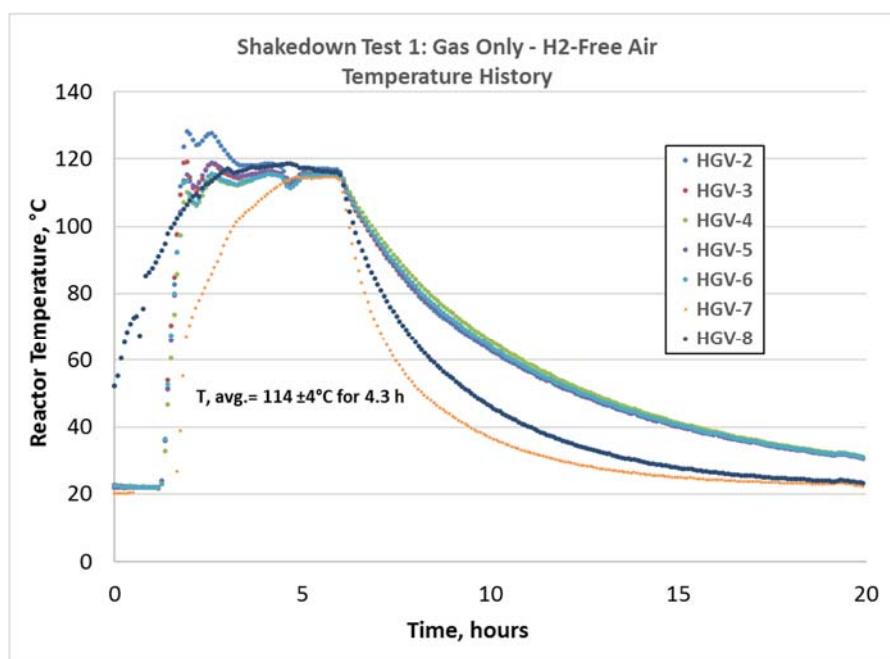
Figure 22. Temperature history of shakedown Test 1
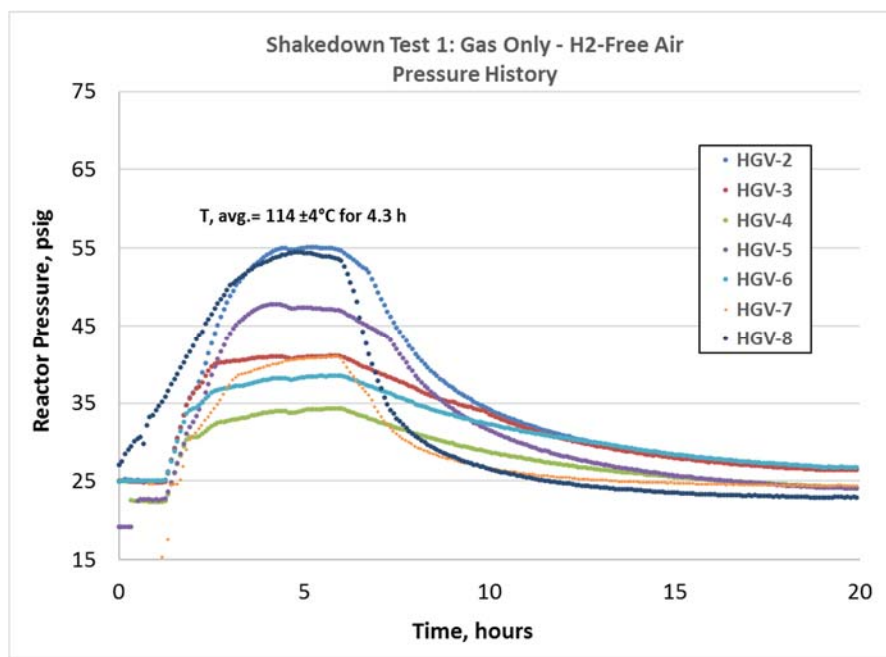
Figure 23. Pressure history of shakedown Test 1
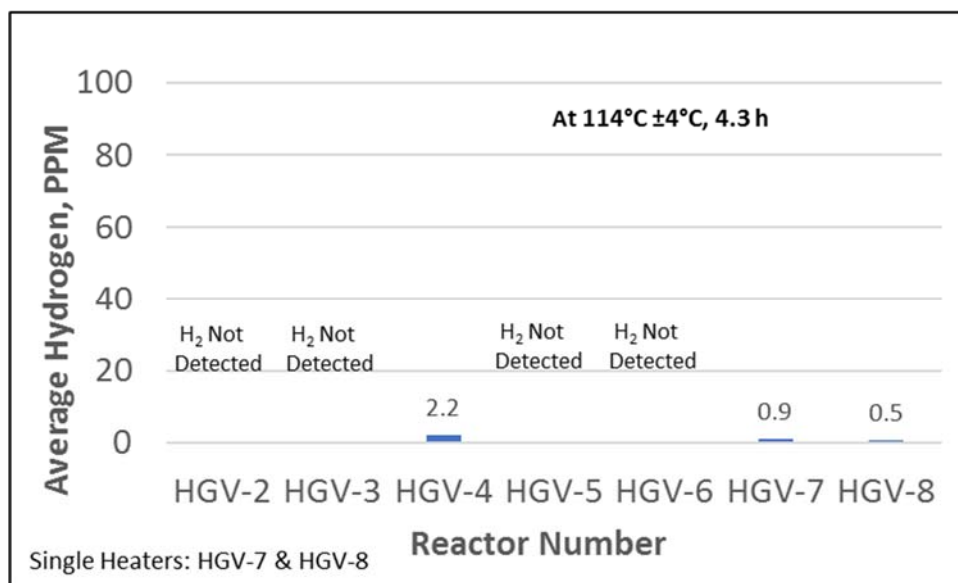
Figure 24. H₂ measurements from shakedown Test 1

Test 2: Gas-only H₂ baseline test at with 10.6 ppm H₂

Once again, for this second shakedown test the seven reactors contained no liquid and were filled with gas. However, this time a calibration gas was used with had a known concentration of H_2 of 10.6 ppm ±0.2 ppm of H_2. The reactors were purged with 15+ reactor volumes of gas, sealed and held at room temperature overnight, when the H_2 was measured. Note, the H_2 was measured directly from the supply cylinder with the GC before the test and the 10.6 ppm was verified. Figure 25 shows that the reactors were held at an average of 20°C for 21 hours. The small temperature fluctuations were from the normal changes in room temperature through the day and night. Figure 26 shows the increase in reactor pressure as the temperature increased. The pressures are different due to the initial pressure, which was close to 15 psig and constant. Figure 27 shows the average of the measured H_2 was 11 ppm for the seven reactors. The 10.6 ppm of H_2 was well bounded within ±0.5 ppm, as indicated on the figure. This test clearly indicates that reactors remained leak tight and impermeable due to the measurement of a known H_2 concentration.
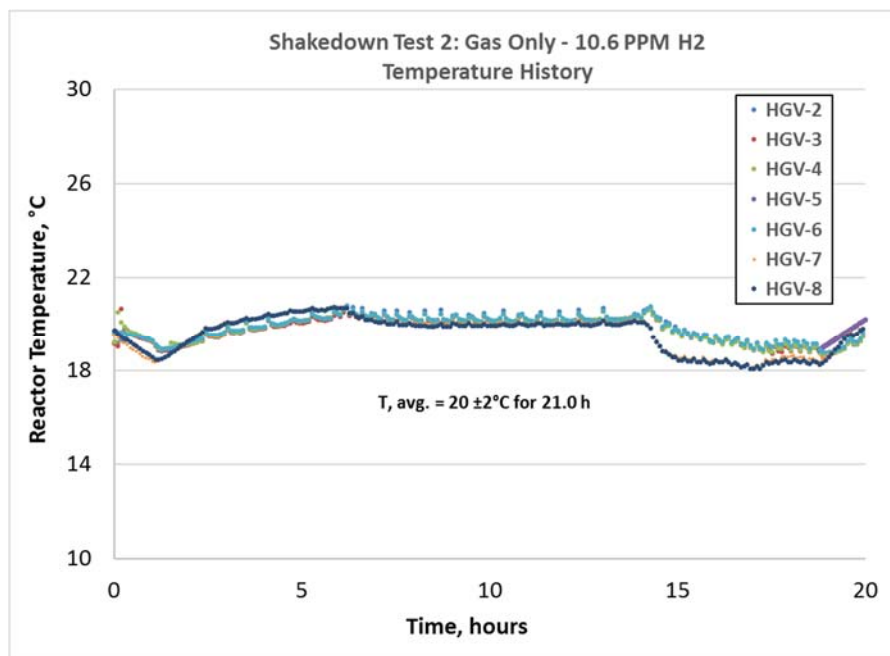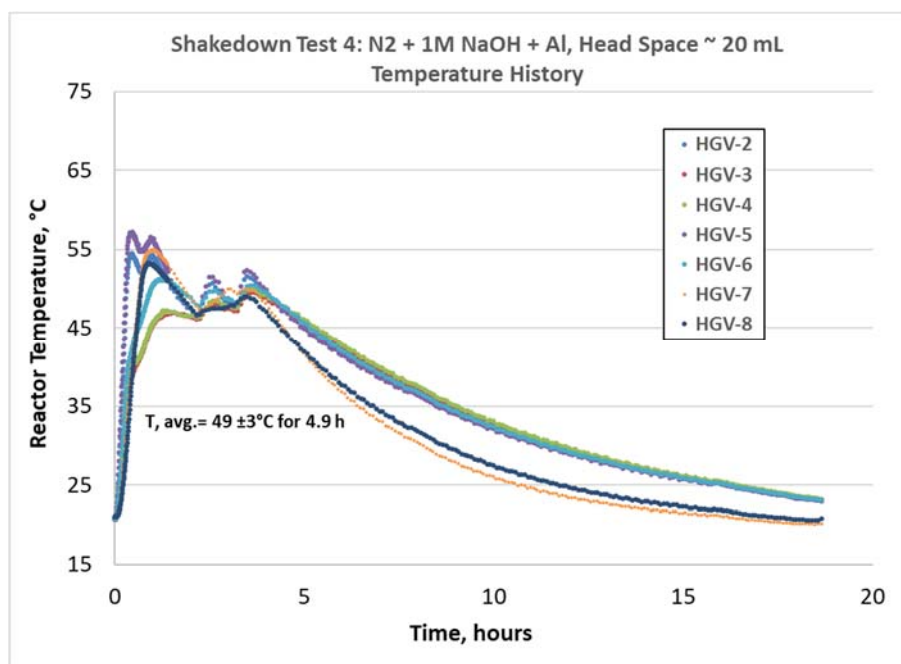

Figure 25. Temperature history of shakedown Test 2
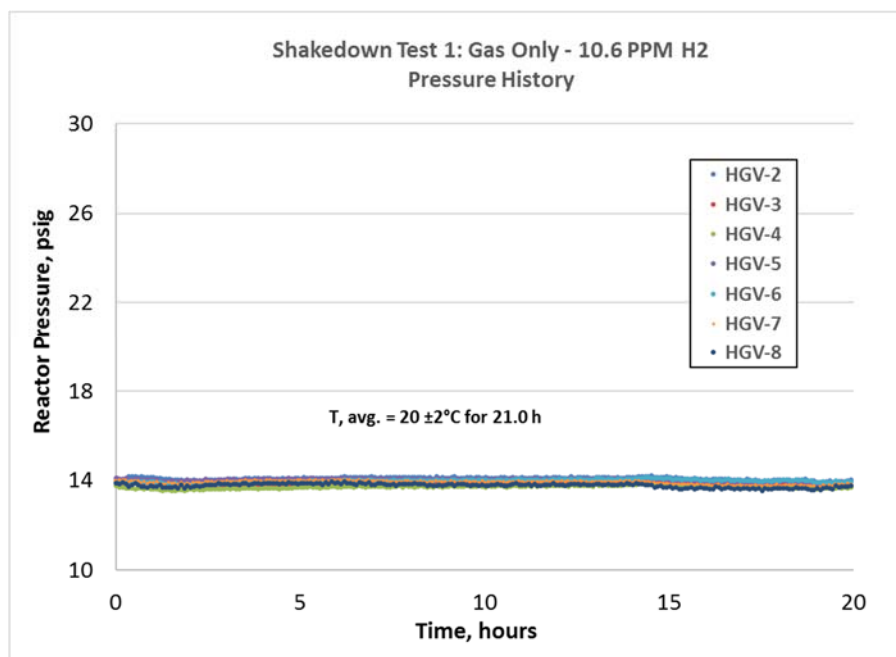
Figure 26. Pressure history of shakedown Test 2
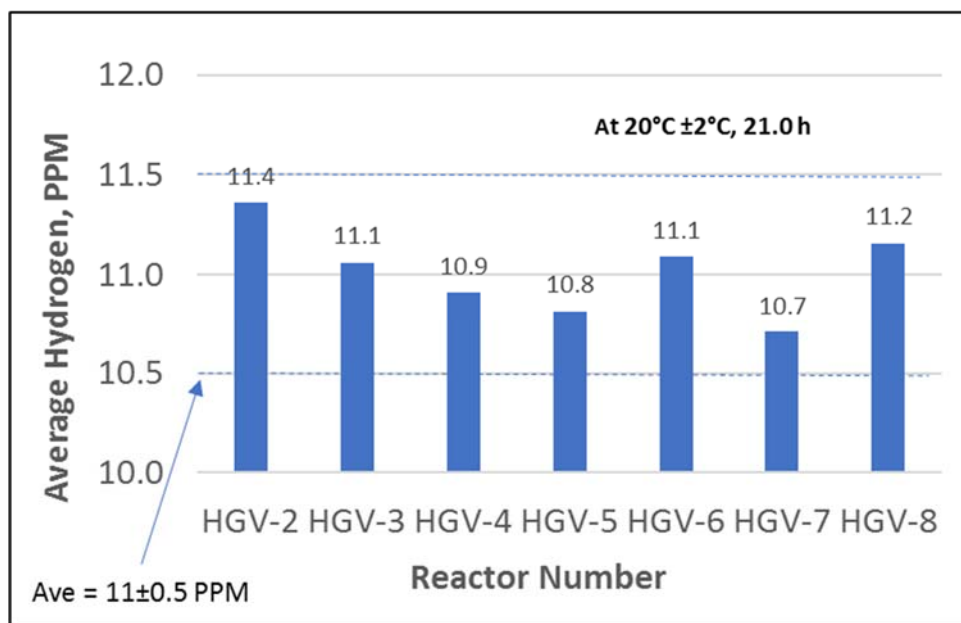
Figure 27. H$_2$ measurements from shakedown Test 2. Reactors filled with 10.6 ppm H$_2$.

Test 3: 1 M NaOH baseline test at 50°C

This shakedown test was the first test with both liquid and gas. This test was a pretest for Test 4, which would dissolve a known mass of pure aluminum in caustic to measure a known amount of H_2 generated, as explained in Section 3.1. While reagent grade caustic was not expected to produce H_2, this was to be demonstrated. Each 195-mL reactor was filled with 175 mL of 1 M NaOH and then was purged with 15+ reactor volumes of H_2-free nitrogen, pressurized to approximately 15 psig, and then sealed. This means the reactor head space was approximately 20 mL (reduced to ~17 mL when considering the 2.715 mL stirrer). The reactors were heated to the target temperture of 50°C, held for more than 4 hours and then allowed to cool overnight, with the H_2 being measured on the following day. Figure 28 shows that the reactors were held at an average of 50°C for more than 4 hours. The initial high temperature from two of the reactors, which was measured on the outside of the reactors, was not expected to have a large effect. As can be seem the internal reactor pressures in Figure 29, internally the system was very stable. Figure 30 shows the H_2 measurements and each value is the average of multiple samples taken from each reactor. No H_2 was expected, but some was measured, which was subsequently discovered to be due to tramp organic material in the caustic, see Section 3.1. However, this small amount of H_2 was not considered significant because Test 4 was expected to produce a H_2 concentration orders of magnitude higher. Because this test had liquid, then a HGR could be obtained and is shown in Figure 31.
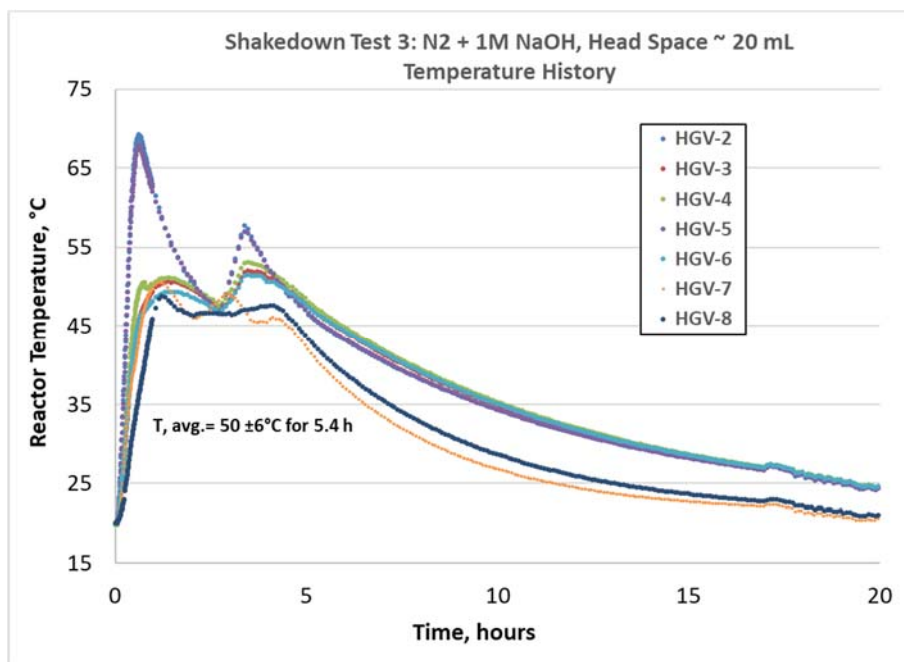
Figure 28. Temperature history of shakedown Test 3
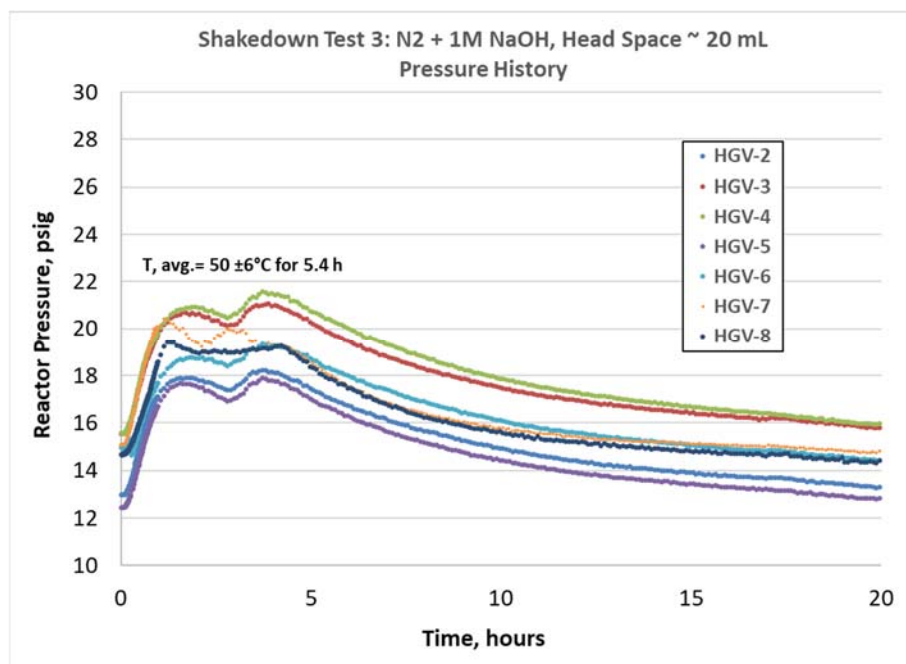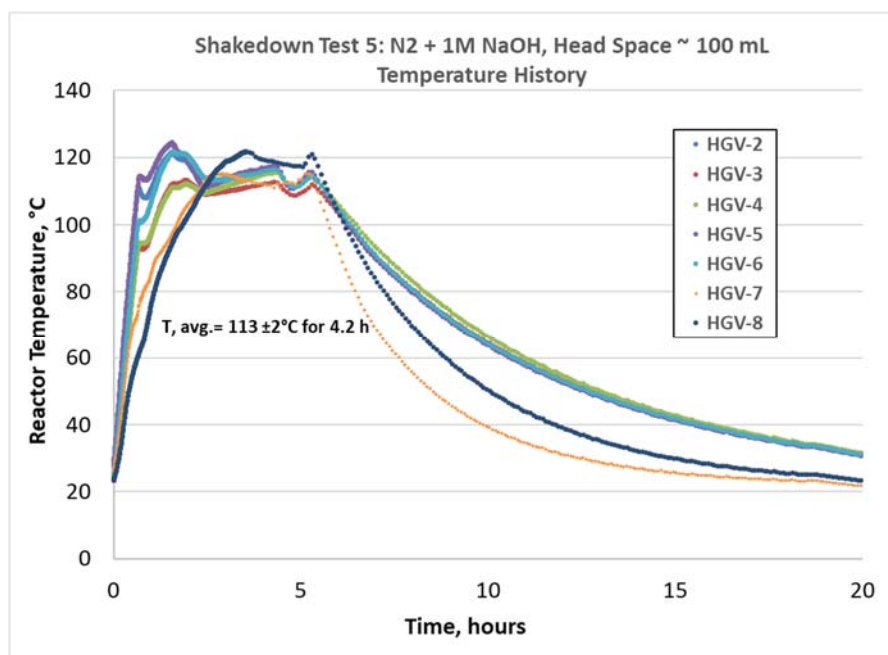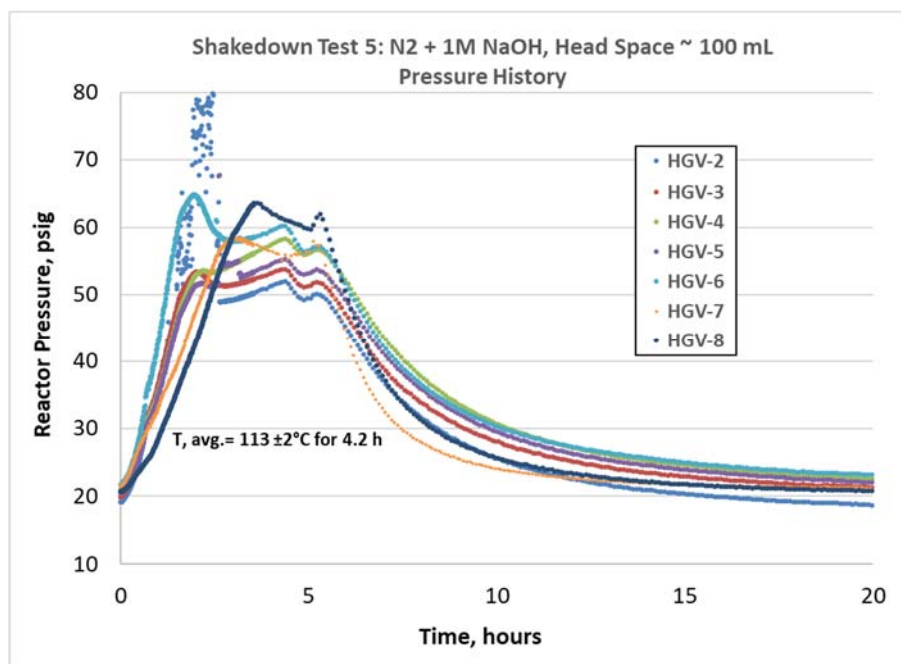
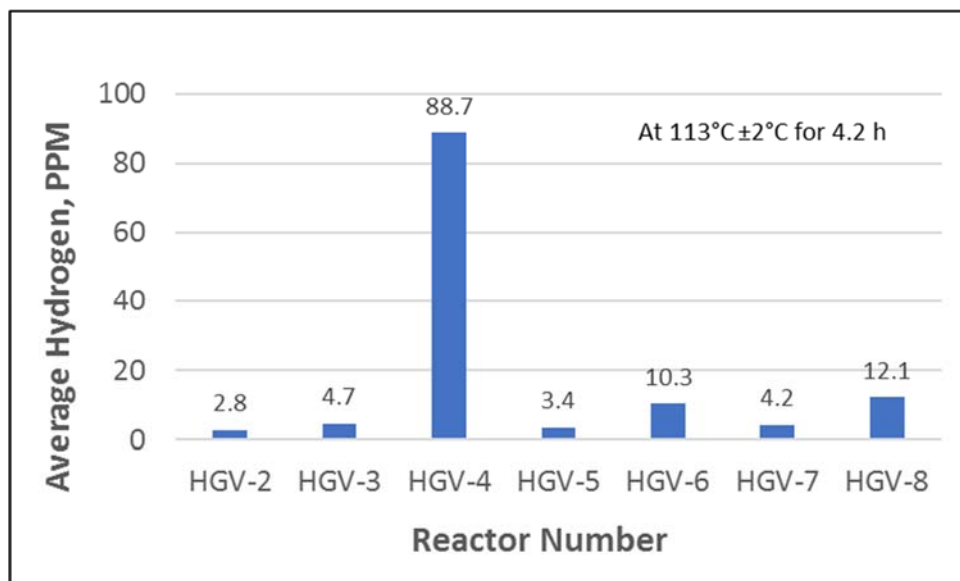**Figure 29. Pressure history of shakedown Test 3**
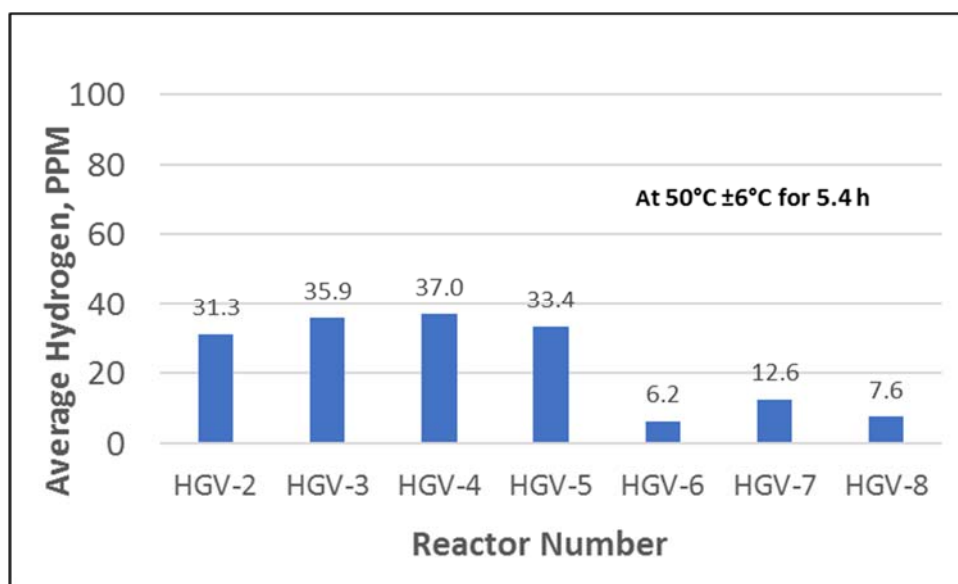
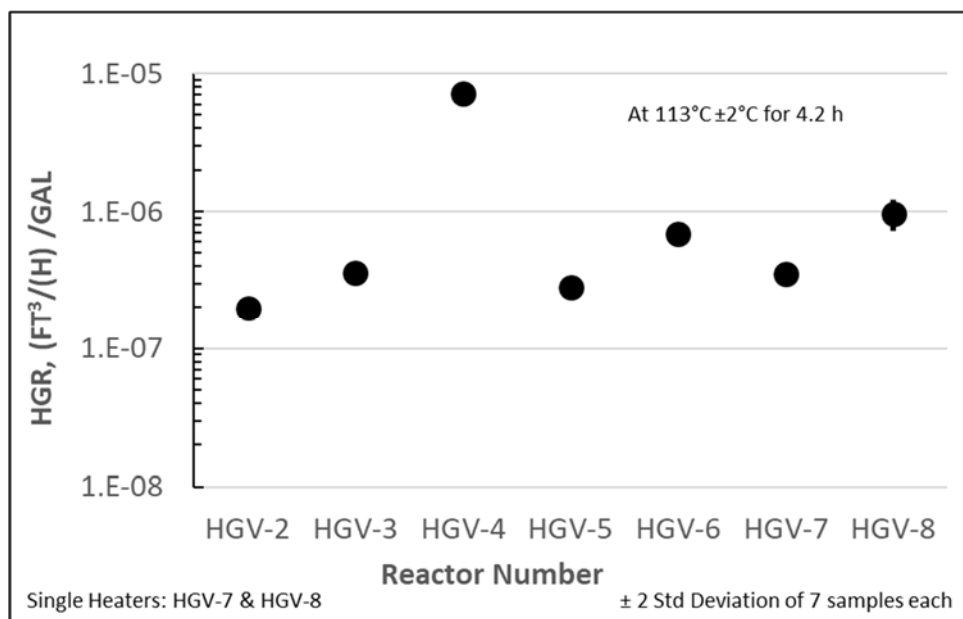**Figure 30. H₂ measurements from shakedown Test 3**
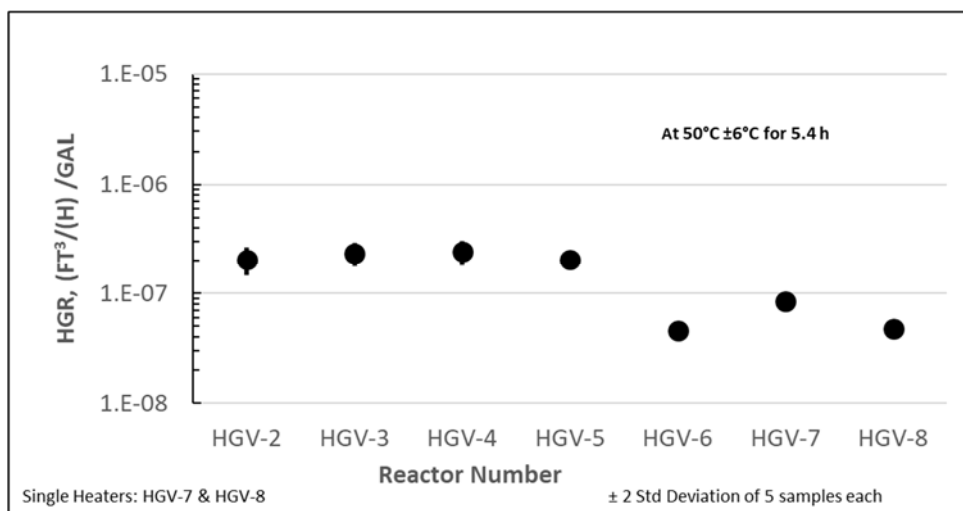
Figure 31. HGR measurements from shakedown Test 3

Test 4: 1 M NaOH aluminum dissolution test at 50°C

This test is a repeat of Test 3, but with the addition of a known mass of aluminum, as discussed in Section 3.1. In fact, the sample caustic used for Test 3 was used for Test 4, which saved time in cleaning and refilling, but the amount H_2 produced in Test 3 from any tramp organics in the caustic was judged as insignificant compared to that expected from aluminum dissolution. Once Test 3 was completed the reactors' liquid introduction port (LIP) was opened and a measured amount of aluminum was introduced, and the LIP was sealed. Once again, each 195-mL reactor was filled with 175 mL of 1 M NaOH and then was purged with 15+ reactor volumes of H_2-free nitrogen, pressurized to approximately 20 psig, and then sealed. This filling and purging process was done at room temperature, so any H_2 produced from aluminum dissolving in the caustic during the few minutes it took to purge and sealed the reactor was thought insignificant. In fact, pre-test evaluations of similar amount aluminum, micrograms, see Table 2, of aluminum in 1 M NaOH was done and it took about 24 hours to dissolve the metal. The reactors were then heated to the target temperture of 50°C, held for more than 4 hours and then allowed to cool overnight, with the H_2 being measured on the following day. Figure 32 shows that the reactors were held at an average of 50°C for more than 4 hours. Figure 33 shows that the starting pressure of near 20 psig increased to about 26 psig during heating. Figure 34 shows the measurement, and each value is the average of multiple samples taken from each reactor. They ranged from just more than 1000 ppmto about 10,000 ppm depending on the mass of metal used. Along side the measurement is an estimate of the aluminum dissolved, based on the equation discussed in Section 3.1. The comparison is not good even though the mass of H_2 created from the aluminum and absorbed into the caustic was considered. A better comparison will be seen for Test 6 The reasons for the poor comparison is the much small size aluminum particle used for Test 4, Table 2, the small head space of 20 mL, instead of the 100 mL for Test 6, and lower temperture of 50°C instead of 120°C (These head spaces were reduced to ~17 mL and ~97 mL, respectively, when considering the 2.715 mL stirrer). Because this test had liquid, then a HGR could be obtained and is shown in Figure 35. Note, the tail (or vertical line) from the top of each data point (circular marker) covers the ragne of the higher value adding 2 standard deviations.
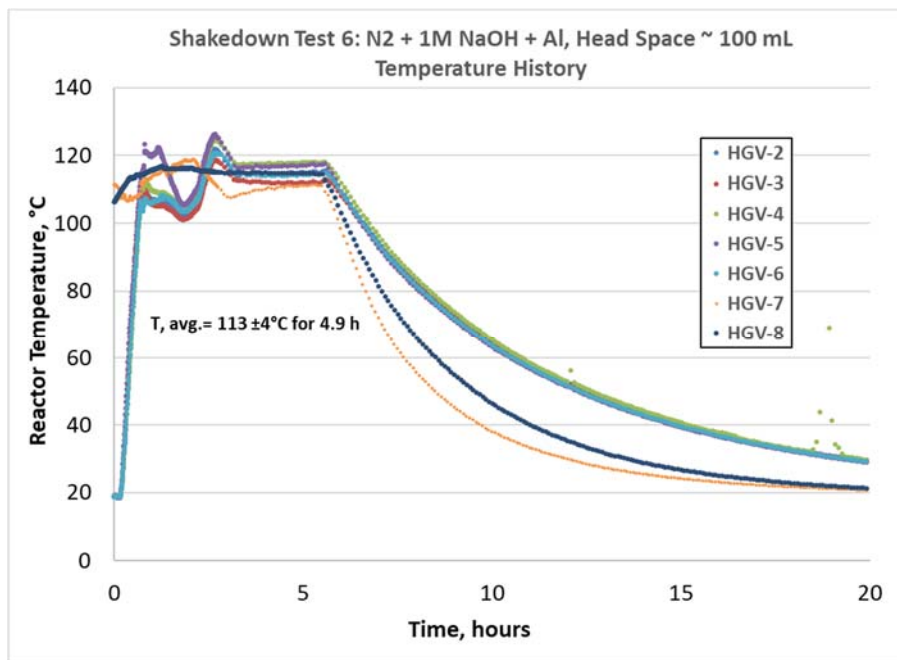

Figure 32. Temperature history of shakedown Test 4
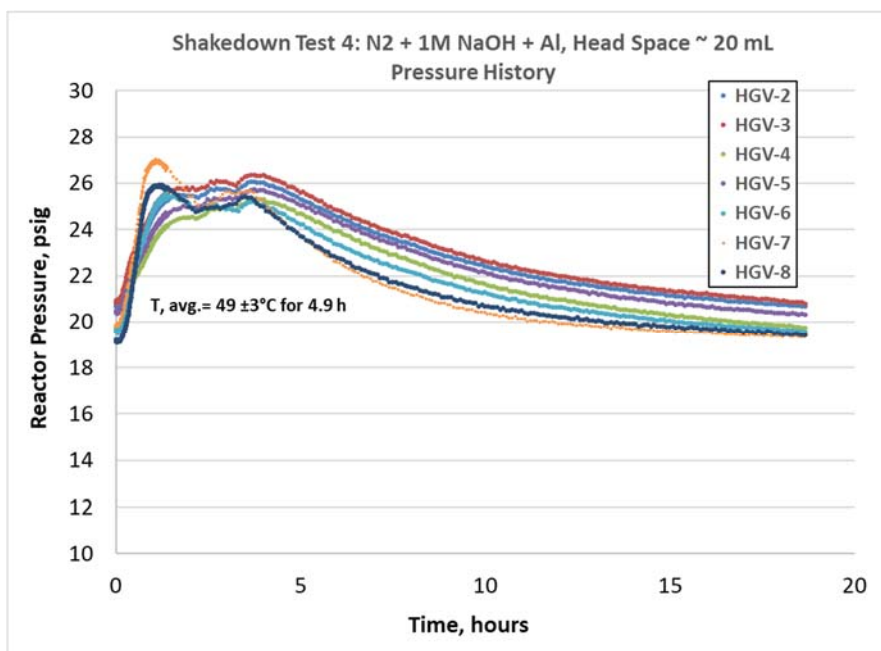
Figure 33. Pressure history of shakedown Test 4
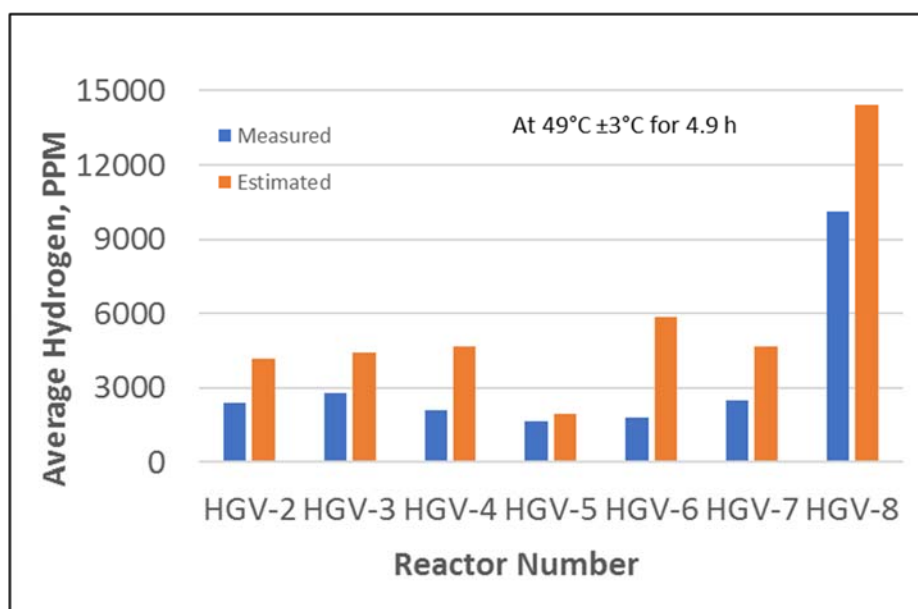
Figure 34. H₂ measurements from shakedown Test 4
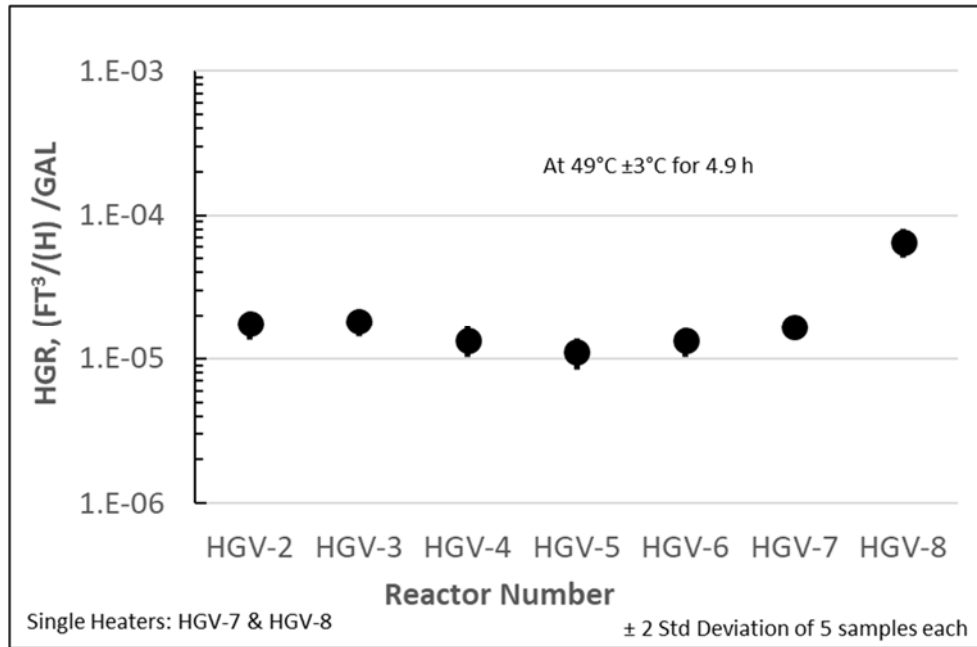
Figure 35. HGR measurements from shakedown Test 4

Test 5: 1 M NaOH baseline test at 120°C

This test, like Test 3, was a control test for Test 6 that dissolved a known mass of pure aluminum in caustic to measure a known amount of H_2 generated, as explained in Section 3.1. Each 195-mL reactor was filled with 95 mL of 1 M NaOH and then was purged with 15+ reactor volumes of H_2-free nitrogen, pressurized to approximately 20 psig, and then sealed. This means the reactor head space was approximately 100 mL. Actually, in filling the volume the target was the gas space, so only the amount of liquid necessary to create a 100 mL head-space volume was used. For example, for reactor HGV-2 the volume, Appendix A, Table 12, is 195.51 mL; therefore 95.51 mL is introduced into the reactor to create a head space of 100 mL (reduced to ~97 mL when considering the 2.715 mL stirrer). The reactors were then heated to the target temperture of 120°C, held for more than 4 hours and then allowed to cool overnight, with the H_2 being measured on the following day. Figure 36 shows that the reactors were held at an average of 113°C for more than 4 hours. The internal reactor pressures are shown in Figure 37 and the high peak of reactor HGV-6 was thought to be a loose connection wire. Once the connection was checked the pressure reading returned to match the others. Figure 38 shows the H_2 measurements and each value is the average of multiple samples taken from each reactor. Like for Test 3, no H_2 was expected but some was measured, especially for HGV-4, but is showed an elevated concentration relative to the other reactors; as cause for this offset has not been determined. However, all the values are assumed to come from tramp organic material in the caustic, Section 3.1. Once again, this small amount of H_2 was not considered significant because Test 6 was expected to produce a H_2 concentration orders of magnitude higher. Because this test had liquid, then a HGR with computed variance bars could be obtained and is shown in Figure 39.

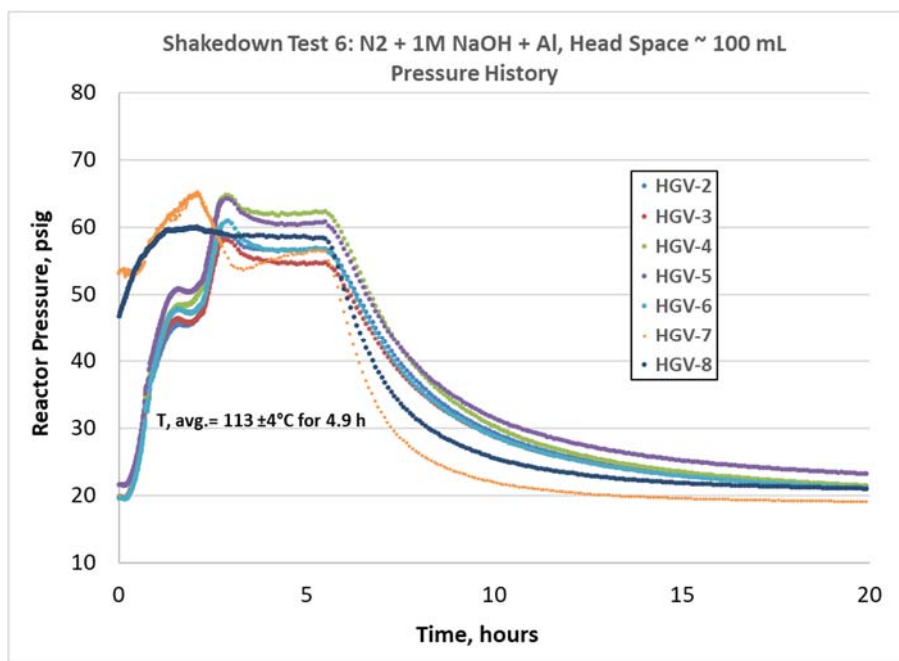**Figure 36. Temperature history of shakedown Test 5**

Figure 37. Pressure history of shakedown Test 5
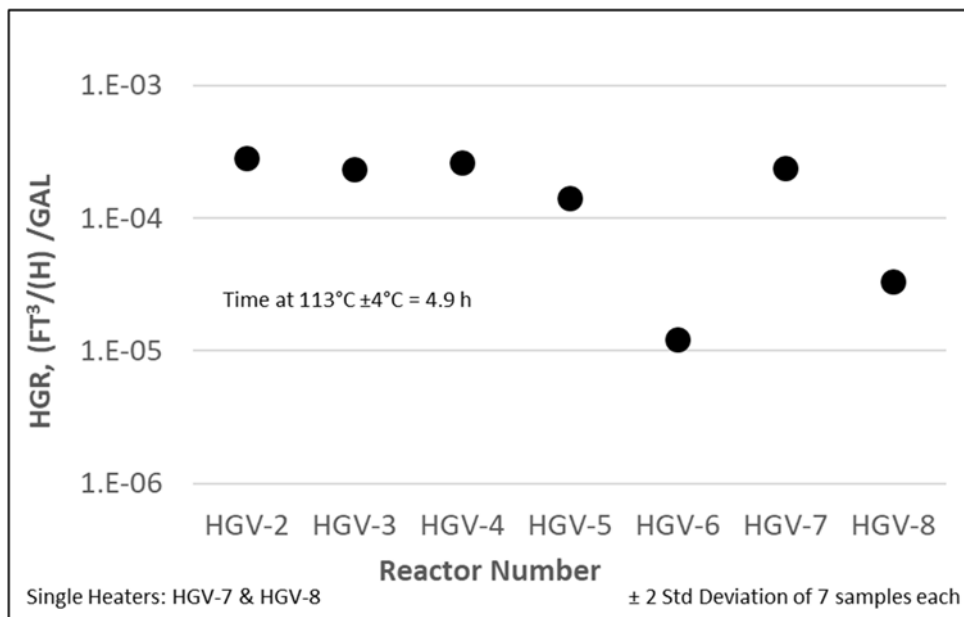

Figure 38. H₂ measurements from shakedown Test 5

Figure 39. HGR measurements from shakedown Test 5

Test 6: 1 M NaOH aluminum dissolution test at 120°C

The final shakedown test is basically a repeat of Test 4, that is, dissolving aluminum in caustic to produce a known amount of H_2. However, the parameters were different with a larger head space, 100 mL (reduced to ~97 mL when considering the 2.715 mL stirrer), larger aluminum masses, Table 2, and at a higher target temperature of 120°C. Once again, the sample caustic used for Test 5 was re-used for Test 6, which saved time in cleaning and refilling, but the small amount of H_2 produced from any tramp organics in the caustic was judged as insignificant compared to that expected from aluminum dissolution. Once Test 5 was completed the reactors' LIP was opened and a measured amount of aluminum was introduced and the LIP was sealed. Then, each 195-mL reactor was purged with 15+ reactor volumes of H_2-free nitrogen, pressurized to approximately 20 psig, and then sealed. This filling and purging process was done at room temperature, so any H_2 produced from aluminum dissolving in the caustic during the few minutes it took to purge and sealed the reactor was thought insignificant. In fact, pre-test evaluations of similar amount aluminum, micrograms, see Table 2, of aluminum in 1 M NaOH was done and it took about 24 hours to dissolve the metal. The reactors were then heated to the target temperture of 120°C, held for more than 4 hours and then allowed to cool overnight, with the H_2 being measured on the following day. Figure 40 shows that the reactors were held at an average of 113°C for more than 4 hours. Figure 41 shows that the starting pressure of near 20 psig increased to about 60 psig during heating. Figure 42 shows the measurement, and each value is the average of multiple samples taken from each reactor. They ranged from just more than 2000 ppm to about 4000 ppm depending on the mass of metal used. Along side the measurement is an estimate of the aluminum dissolved based on the equation discussed in Section 3.1. Except for HGV-5 the comparison is much better than made for Test 4 and the mass of H_2 dissolved in the caustic was considered. Neglect the results for HGV-6, which the aluminum was not inserted, and HGV-8, where the head space was accidentally vented, which lost the sample. The accidental ommission of the aluminum was determined because the mass was found after the test. The particles were so small that they were hard to see by eye. It is believed something was inserted, but it was not the aluminum. Because this test had liquid, then a HGR could be obtained and is shown in Figure 43 with the 2 standard deviation variance.

Figure 40. Temperature history of shakedown Test 6

Figure 41. Pressure history of shakedown Test 6
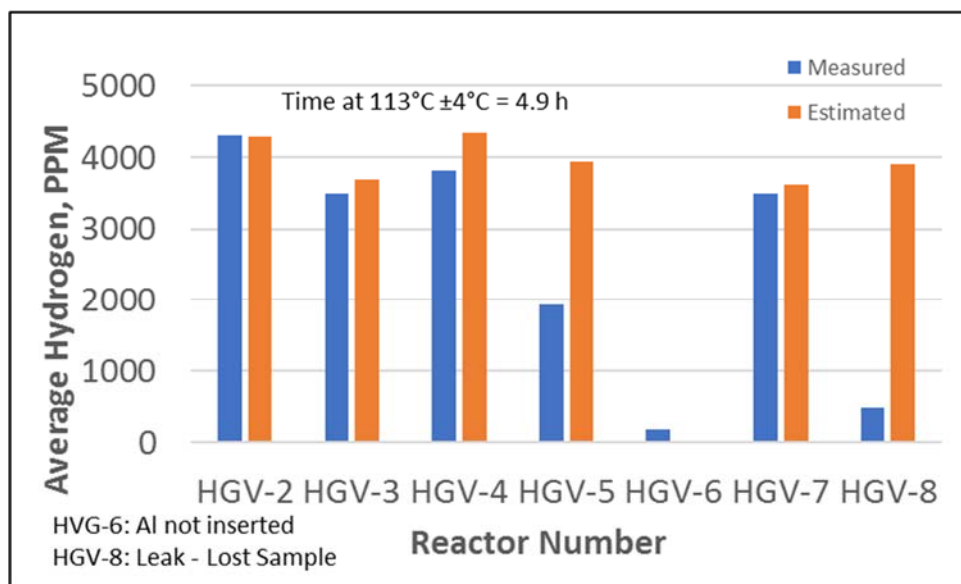
Figure 42. H₂ measurements from shakedown Test 6

Figure 43. H$_2$ generation ate measurements from shakedown Test 6

Appendix G: Simulant Individual Test Results

Simulant testing included four planned campaigns, after which a fifth was included to repeat some tests with important spikes over a 6-day period, instead of the 4 hours used for most of the simulant tests. The goals of simulant testing were to perfect operations before starting radioactive work, have a good idea of H_2 production with and without spikes, and to demonstrate measurements of HGR as low as $1.0E10^{-10}$ (ft^3/h)/gal. This appendix described each test.

The following data for each test will be presented by the measurements of: Temperature History, Pressure History, and the H_2, which was obtained during the gas sampling of each reactor after it returned to room temperature. This information, along with reactor specifics, is used to create the last graph, which shows the result of a calculation of HGR. That calculation is adjusted to a pressure of 1 atmosphere (14.7 psia) and a temperature of 25°C. That is, for the HGR calculation, the sampling initial pressure, which was usually close to 20 psig, and temperature, which was usually between 22°C to 28°C, were adjusted so all the graphical data are adjusted to 1 atm and 25°C. The equation used for HGR was:

[[(Head Space Volume, ft^3) • A • H_2 Measured, ppm / 1000000] / (Test Time, hours)] / Volume Liquid, gal

Where A =

[Pinitial sample / Pstandard] [Tstandard/Tsampling] =

[(Initial Sample Head Pressure, psig + 14.7 psia) / 14.7 psia] [298 K / (T°C at sampling+273 K)]

With Pstandard = 14.7 psia and Tstandard = 25°C

Test 1: Simulant test at 25•C with 20 mL head and 120•C with 100 mL head – No Spikes

Test 1 is further subdivided into two tests. Test 1-1 and 1-2 to repeat the test with H_2-free air after testing with N^2. Originally this was to be a single test with a few reactors having nitrogen and a few with air. However, a mistake was made when all the reactors were filled with nitrogen for Test 1, so instead of starting over, Test 1 became Test 1-1 with nitrogen, then it was repeated with air as Test 1-2. The advantage was more data points that could used to better study the variability among the reactors.

Test 1-1: Simulant test at 25•C, 100•C, and other conditions listed in Table 22

Table 22. Simulant Test 1-1

Test Spike Type	Reactor Used	Fill Gas	Nominal Temp.,°C	Amount of liquid, mL	Duration
None	HGV-7	N_2	25	180	> 24 hours
None	HGV-8	N_2	25	180	> 24 hours
None	HGV-2	N_2	120	100	> 4 hours
None	HGV-3	N_2	120	100	> 4 hours
None	HGV-4	N_2	120	100	> 4 hours
None	HGV-5	N_2	120	100	> 4 hours
None	HGV-6	N_2	120	100	> 4 hours

This test set has two temperatures because the original intent was to conduct two tests for a longer (6-day) period. However, after Test 1 was split into Test 1-1 (with N_2) and Test 1-2 (with Air), then the two room temperature reactors were measured for H_2 with all the other reactors in Test 1-1, so that the long-term test (Test 1-2 (for 6 days) could be performed with H_2-free air, as originally planned. Test 1 was planned without any spike so a good baseline could be developed for H_2 generation from simulant without spikes.

The preparation of each test was very similar. Each 195-mL reactor was filled with 95 mL of simulant and then was purged with 15+ reactor volumes of nitrogen, pressurized to approximately 20 psig, and then sealed. This means the reactor head space was approximately 100 mL, but when considering the 2.715 mL stir bar the space was closer to 97 mL. Actually, in filling the target volume was the gas space, so only the amount of liquid necessary to create a 100 mL volume was used. For example, for reactor HGV-2 the volume, Appendix A, Table 12, is 195.51 mL; therefore 95.51 mL is introduced into the reactor to create a head space of 100 mL. The two lower temperature reactors (i.e., HGV-7 and HGV-8) had only a 20 mL head space (reduce to approximately 17 mL when considering the volume of the stir bar); they with filled with ~175 mL of simulant. These two reactors were chosen for the room termperature test because they were located on individual stirrer/hotplates, where as the other five reactors were bunched together on a single large stirrer/hotplate. Except for the two room-temperature reactors, the reactors were then heated to the target temperture of 120°C, held for more than 4 hours and then allowed to cool overnight, with the H_2 being measured on the following day. Figure 44 shows that the reactors we heated to an average of 114°C and held for more than 4 hours. The two reactors at room temperature stated sealed for approximately 25 hours, when the H_2 from all seven reactors was sampled. Figure 45 shows the how the pressures increased from about 20 to 50 psig, basically due to water vapor. Figure 46 shows the H_2 results, which are barely quantifiable. The five heated reactors had concentration near 5 ppm, but the two unheated reactors demonstrated H_2 that was on the borderline of being detectable, with a detection limit of 1 ppm. Figure 47 shows the HGR and for heated reactors they all demonstrated about 10^{-7} (ft^3/h)/gal, while the unheated reactors more than two orders of magnitude lower.
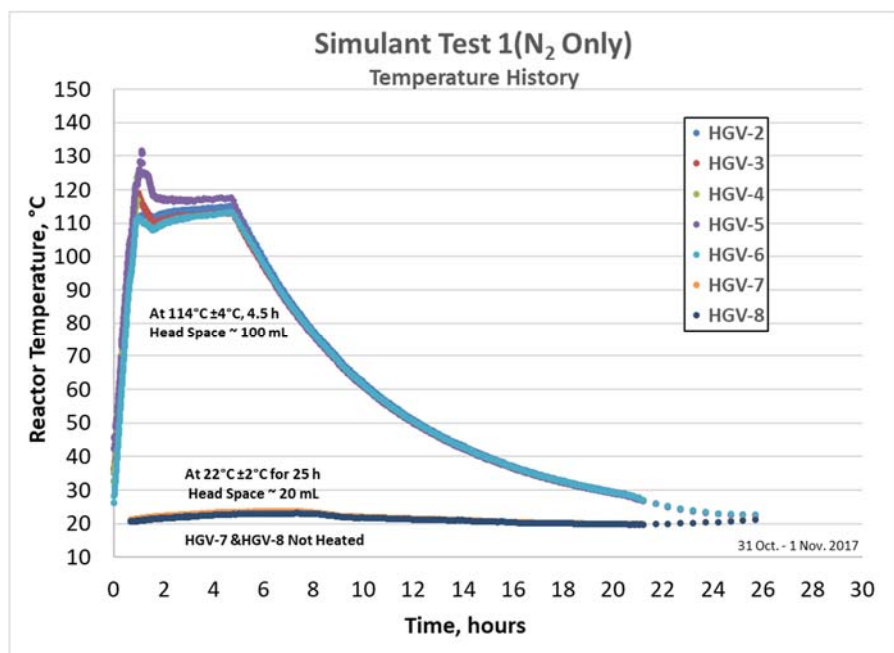
Figure 44. Temperature history of simulant Test 1-1
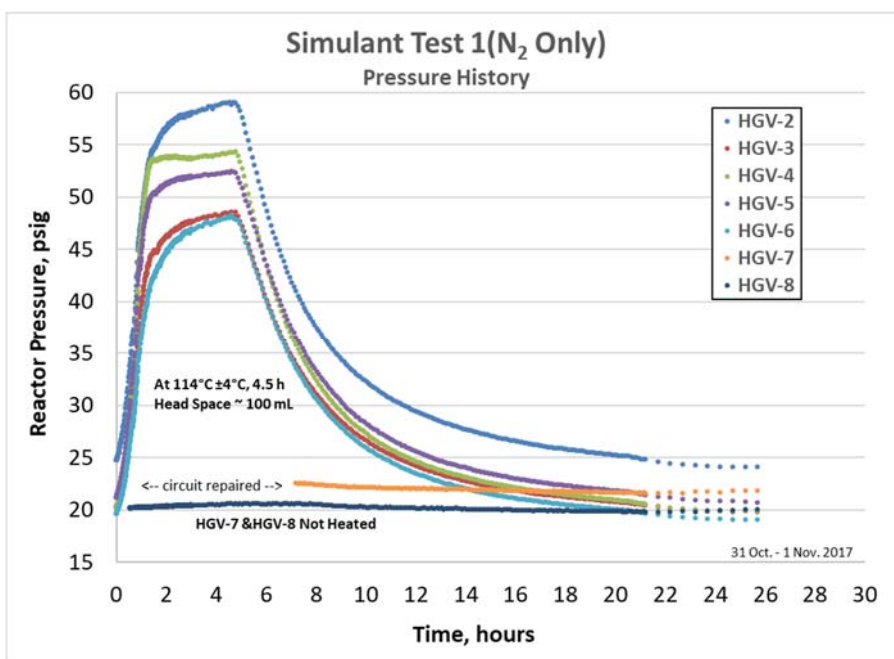
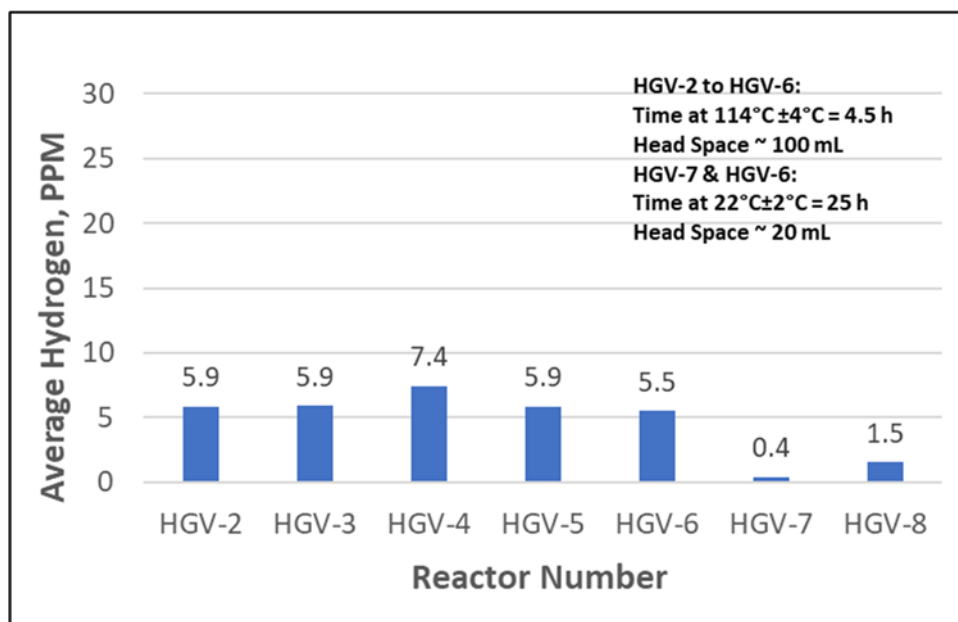**Figure 45. Pressure history of simulant Test 1-1**

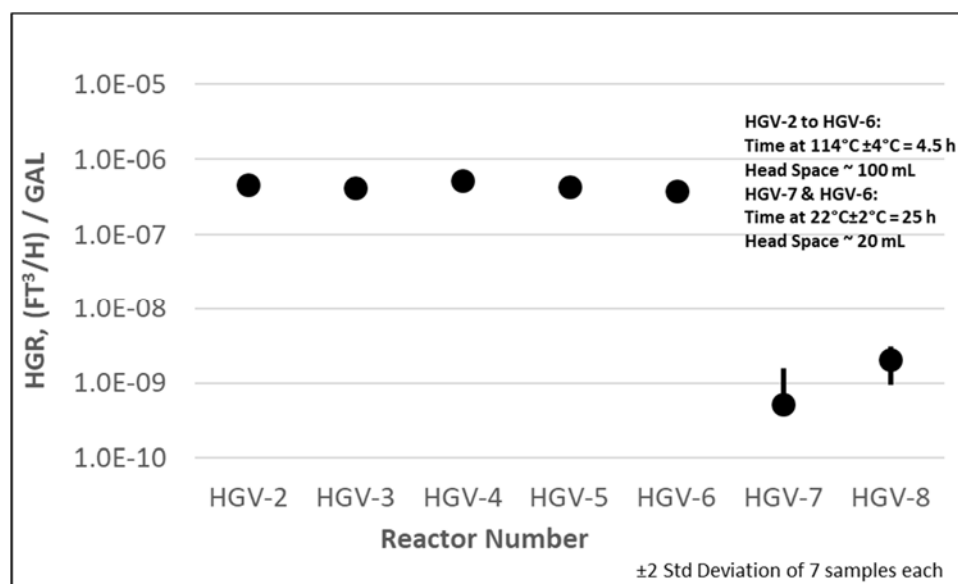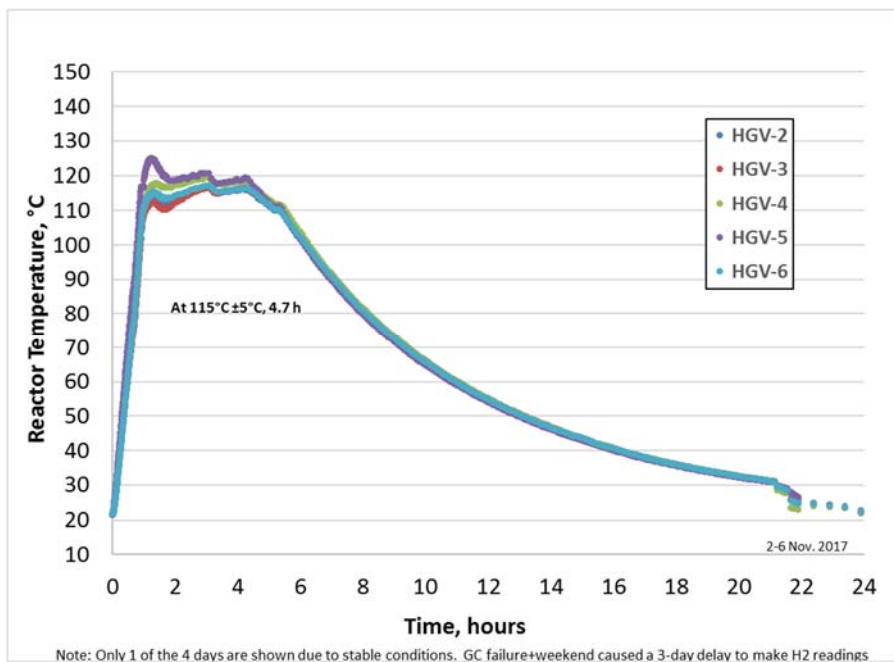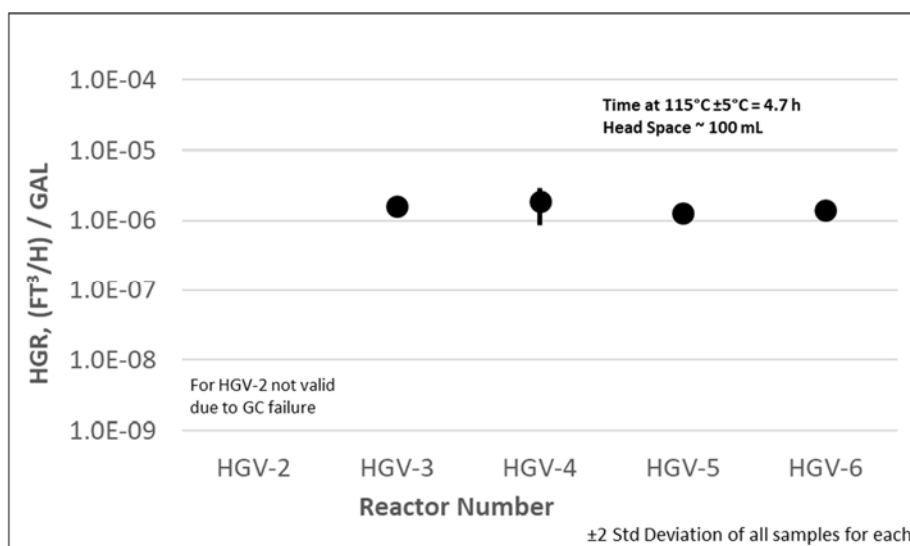**Figure 46. H$_2$ measurements from simulant Test 1-1**

Figure 47. HGR measurements from simulant Test 1-1

Test 1-2: Simulant test at 120°C and other conditions listed in Table 23 for 4 hours

Table 23. Simulant Test 1-2 (4 hours) and Test 1-2 (6 days)

Test Spike Type	Reactor Used	Fill Gas	Nominal Temp.,°C	Amount of liquid, mL	Duration
None	HGV-7	Air-No H_2	25	180	> 6 days
None	HGV-8	Air-No H_2	25	180	> 6 days
None	HGV-2	Air-No H_2	120	100	> 4 hours
None	HGV-3	Air-No H_2	120	100	> 4 hours
None	HGV-4	Air-No H_2	120	100	> 4 hours
None	HGV-5	Air-No H_2	120	100	> 4 hours
None	HGV-6	Air-No H_2	120	100	> 4 hours

Test 1-2 was a repeat of Test 1-1 with one exception: the head space gas was H_2-free air. To start this test the five reactors from Test 1-1 were emptied and refilled with fresh simulant that was not heated. However, after sampling reactors HGV-7 and HGV-8 in Test 1-1for H_2 they were simply re-purged with air to start the Test 1-2 conditions with the same solution since they were never heated.

The preparation of each test was very similar. Each 195-mL reactor was filled with 95 mL of simulant and then was purged with 15+ reactor volumes of H_2-free air, pressurized to approximately 20 psig, and then sealed. This means the reactor head space was approximately 100 mL (reduced to ~97 mL due to the stir bar). As just stated, the two long-term reactors (i.e., HGV-7 and HGV-8) with a 20 mL head space were simply repurged, but with the H_2-free air. Except for the two room-temperature reactors, the reactors were then heated to the target temperture of 120°C, held for more than 4 hours and then allowed to cool overnight, with the H_2 being measured on the following day. Figure 48 shows that the reactors were heated to an average of 115°C and held for more than 4 hours. Note, the graph only shows the five heated reactors because the two unheated reactors will be discussed separated, due to the longer test period of 6 days. Figure 49 shows the how the pressures increased from about 20 to 50 psig, basically due to water vapor. Figure 50 shows the H_2 results and while quantifiable, the magnitude was not large, near 20 ppm for all the reactors except HGV-2. When sample began there was a GC failure causing the head space of that reactor to empty, thus losing the reading. Figure 51 shows the HGR and for heated reactors they all demonstrated about 10^{-6} (ft^3/h)/gal.

Figure 48. Temperature history of simulant Test 1-2 (4 hour)
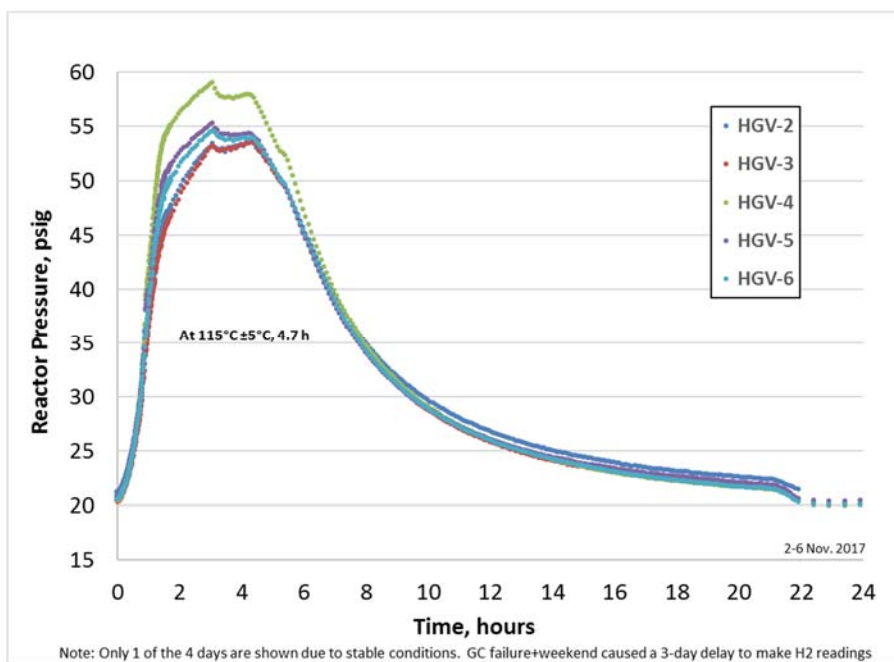
Figure 49. Pressure history of simulant Test 1-1 (4 hours)
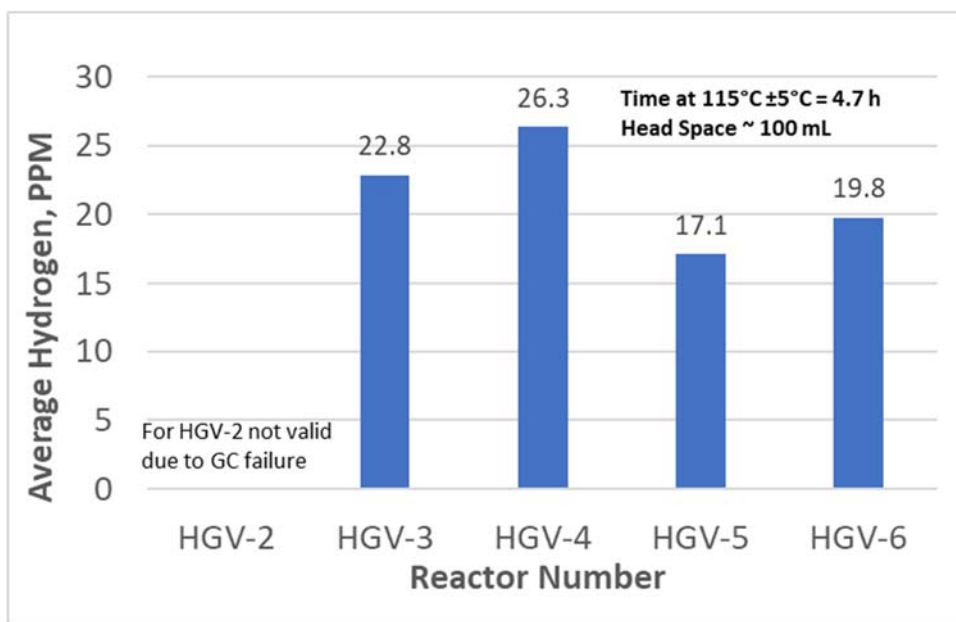
Figure 50. H₂ measurements from simulant Test 1-2 (4 hours)

Figure 51. HGR measurements from simulant Test 1-2 (4 hours)

Test 1-2: Simulant test at 25°C and other conditions listed in Table 23 for 6 days

This section was separated from preceding section because of the longer term of the test, 6 days, instead of 4 hours. Figure 52 shows that the reactors were held at room temperature and had an average temperature of 24°C over almost 8 days (182 hours). Figure 53 shows the gauge pressure of about 20 psig. This clearly indicated the reactor seals worked well. Note, the gaps in the data were caused when the DAS to these two reactors needed to be disconnect for concurrent heated tests with the other 5 reactors. Furthermore, the DAS circuit for HGV-7 needed repair. However, the reactors themselves continued undisturbed and when the signals were re-established the temperature and pressures were still steady and at the target values. Figure 54 shows the H_2 results and while quantifiable, the magnitude was not large, with only 4 ppm for one reactor and 11 ppm for the other. These two values are measurably different but at these very sensitive and low levels the difference is probably not important. However, Figure 55 shows the HGR values met one of the goals of these tests; that is, rates on the order of 10^{-10} (ft^3/h)/gal.
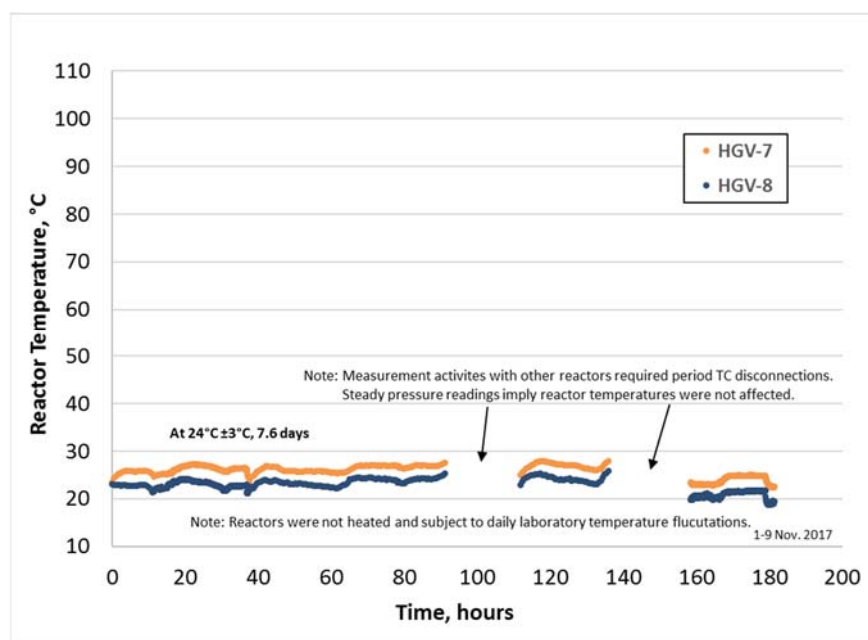
Figure 52. Pressure history of simulant Test 1-2 (6 days)
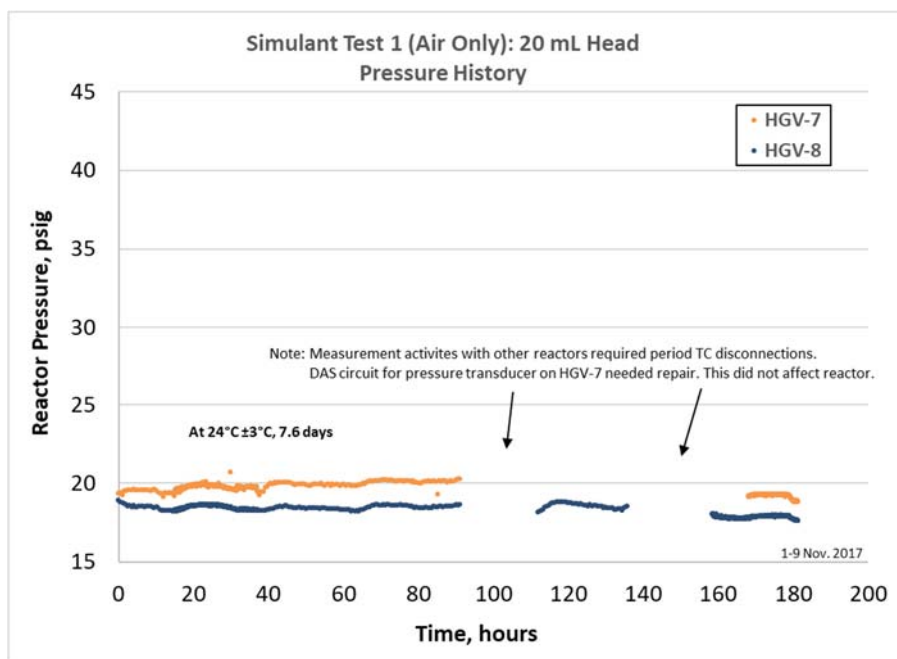
Figure 53. Pressure history of simulant Test 1-2 (6 days)
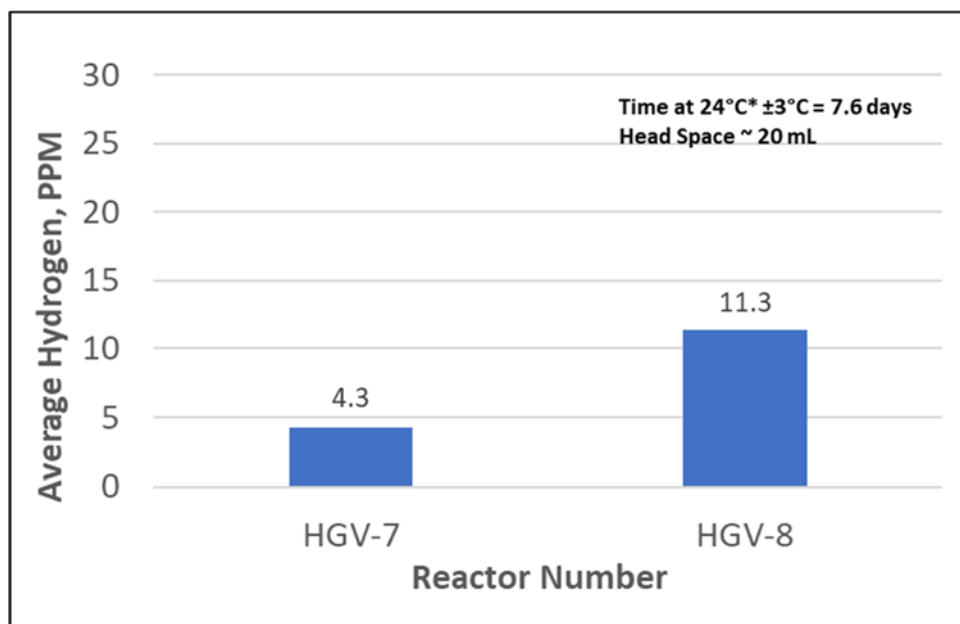
Figure 54. H$_2$ measurements from shakedown Test 1-2 (6 days)
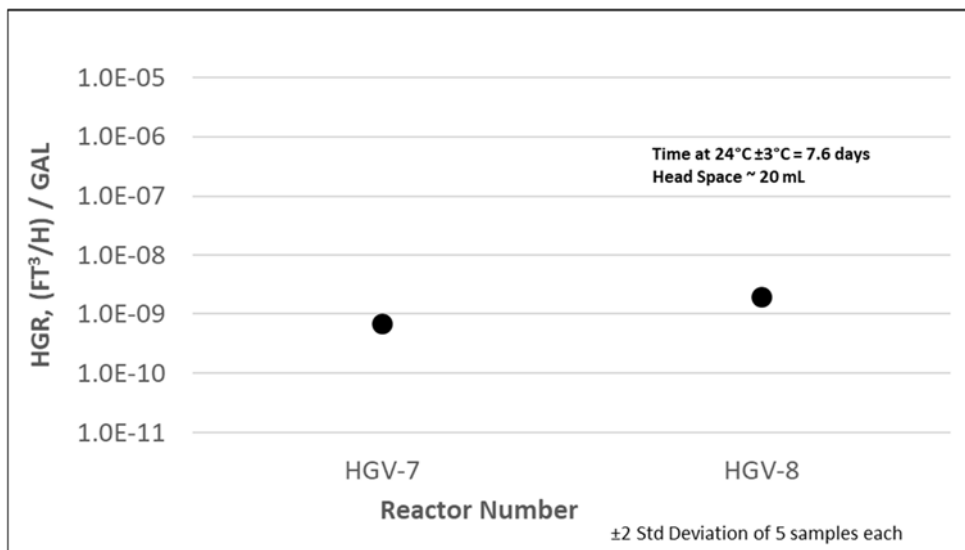
Figure 55. HGR measurements from simulant Test 1-2 (6 days)

Test 2: Simulant test at 100°C and other conditions listed in Table 24

Table 24. Simulant Test 2

Spike Type	Reactor Used	Fill Gas	Amount of liquid, mL	Duration
Formate anoxic	HGV-2	N_2	100	> 4 hours
Formate anoxic #2	HGV-3	N_2	100	> 4 hours
Formate oxic	HGV-4	Air, No H_2	100	> 4 hours
Formate oxic #2	HGV-5	Air, No H_2	100	> 4 hours
Blank - Control	HGV-6	Air, No H_2	100	> 4 hours

With Test 1 complete Test 2 was the first test using spike material, specifically formate, in both oxic and anoxic atmospheres. The long-term test, Test 1-2 (6 days) was ongoing when Test 2 began, so this is the reason only five reactors were used. The preparation of each test was very similar to that for previous tests, but a new batch of simulant was made specifically for this test which was spiked with sodium formate so it would contain 247 mg/L of TOC. Once the spiked simulant was ready, four of the 195-mL reactors were filled with 95 mL of the solution and then two were purged nitrogen and two with H_2-free air. The purge for each was with 15+ reactor volumes and then sealed at approximately 20 psig. This means the reactor head space was approximately 100 mL(reduced to 97 mL due to the stir bar). The reactors were then heated to the target temperture of 100°C, held for more than 4 hours, and then allowed to cool overnight, with the H_2 being measured on the following day. Figure 56 shows that the reactors were heated to an average of 93°C and held for more than 5 hours. Figure 57 shows the how the pressures increased from about 20 to 40 psig, basically due to water vapor. Figure 58 shows the H_2 results and while quantifiable, the magnitudes were not large, between 3 and 5 ppm. These data imply that formate had no significant impact on the H_2 generation, as compared to no spike. Figure 59 shows the HGR and for the reactors at about 10^{-7} (ft^3/h)/gal.
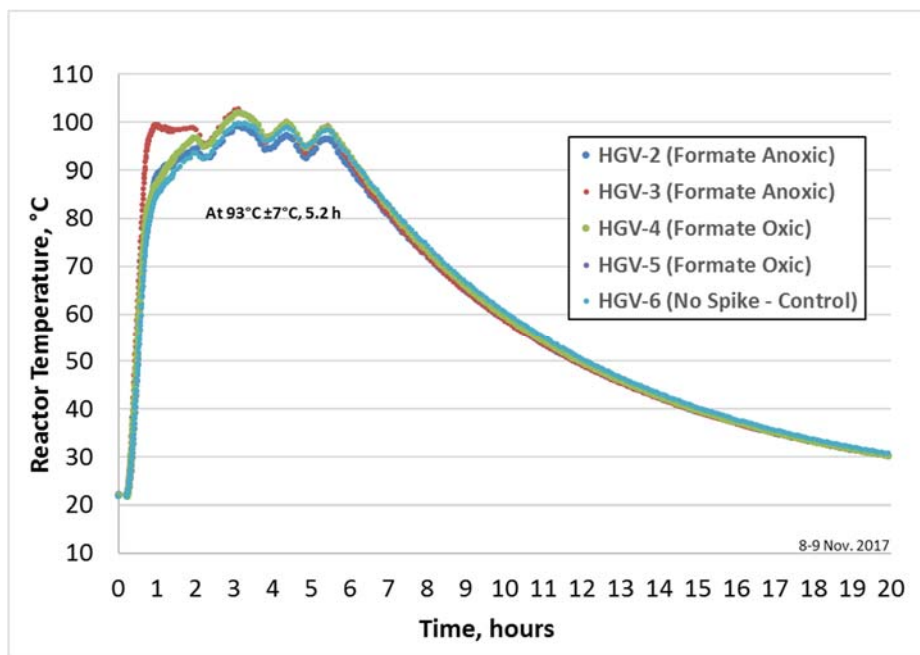
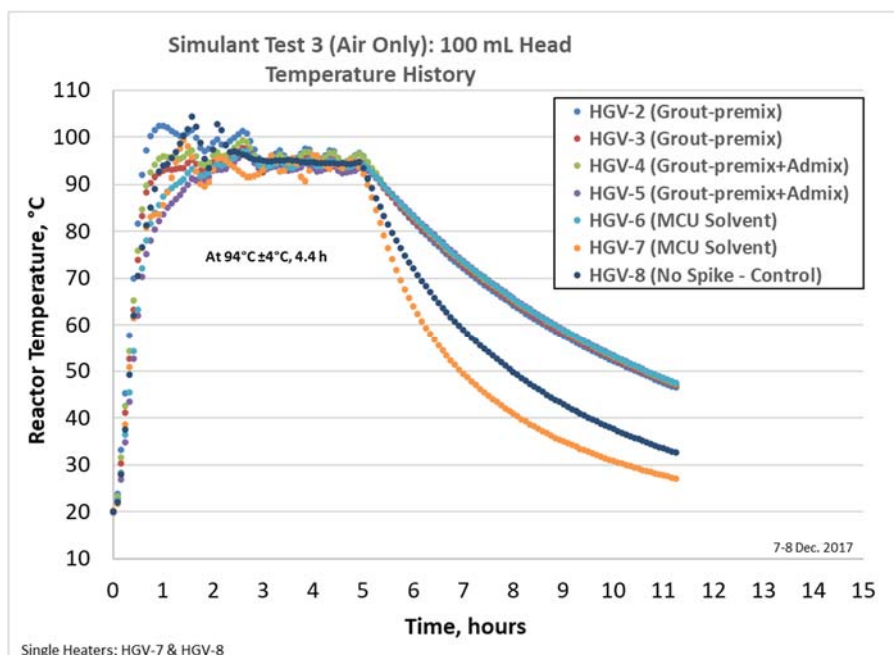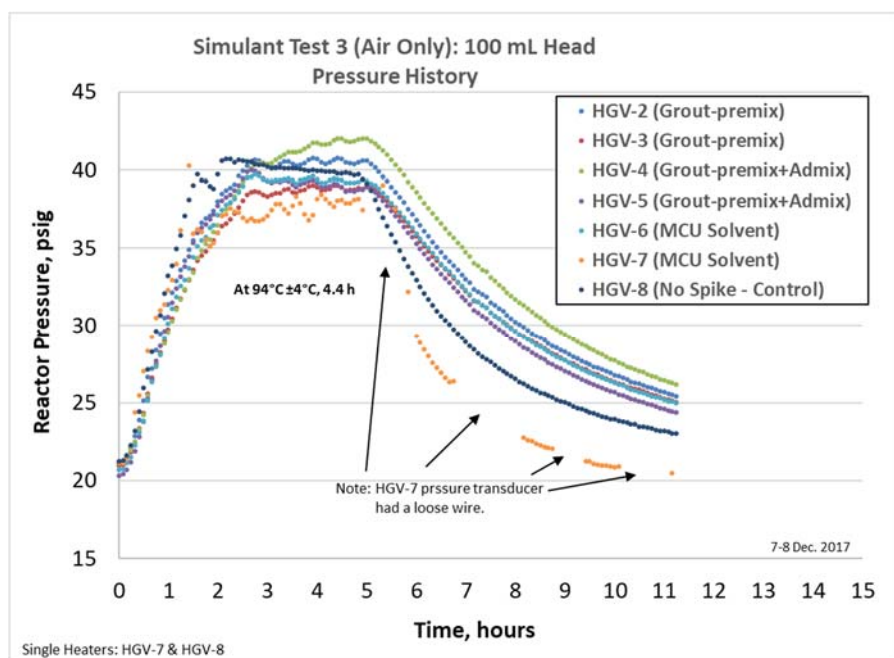**Figure 56. Temperature history of simulant Test 2**
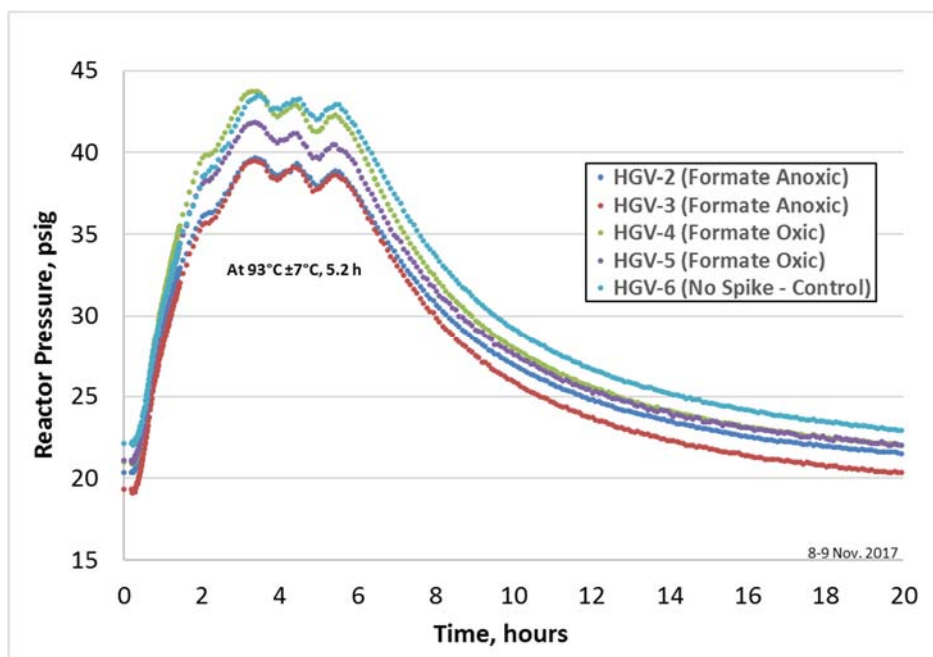
Figure 57. Pressure history of simulant Test 2
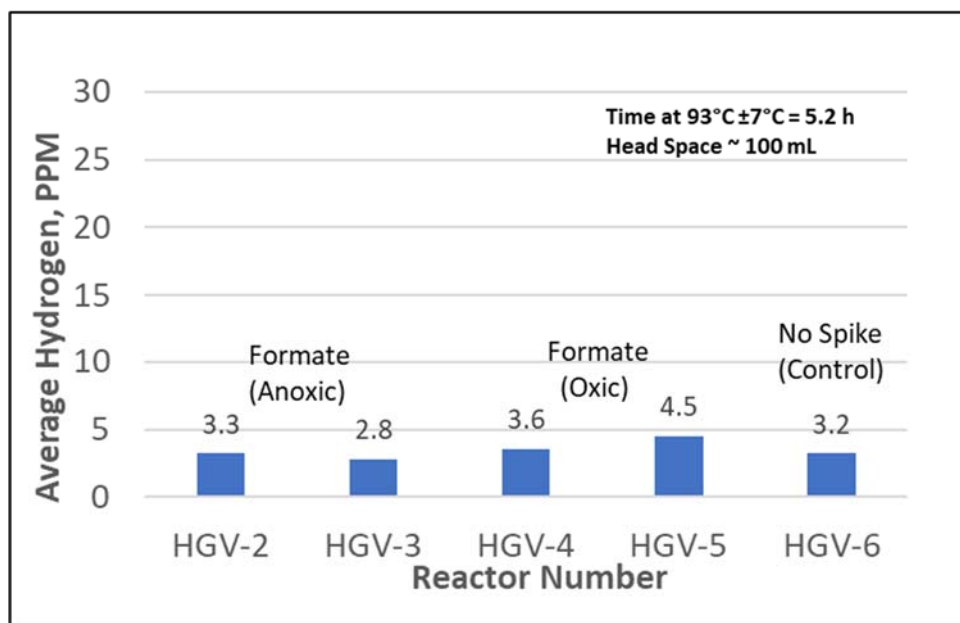
Figure 58. H₂ measurements from simulant Test 2
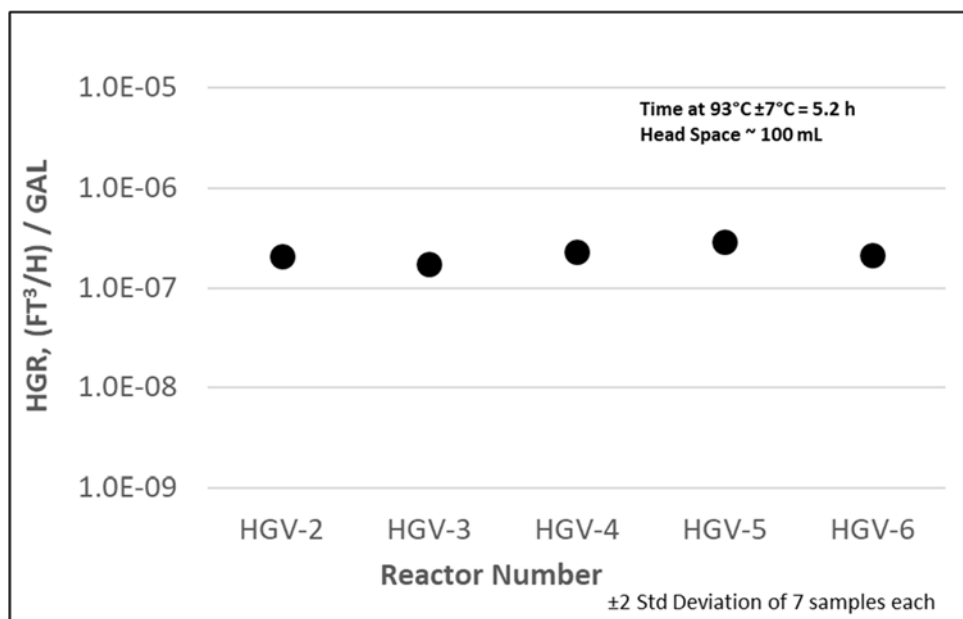
Figure 59. HGR measurements from simulant Test 2

Test 3: Simulant test at 100°C and other conditions listed in Table 25

Table 25. Simulant Test 3

Spike Type	Reactor Used	Fill Gas	Amount of liquid, mL	Duration
Grout-premix	HGV-2	Air, No H_2	100	> 4 hours
Grout-premix #2	HGV-3	Air, No H_2	100	> 4 hours
Grout-premix + Admix	HGV-4	Air, No H_2	100	> 4 hours
Grout-premix + Admix #2	HGV-5	Air, No H_2	100	> 4 hours
MCU oxic	HGV-6	Air, No H_2	100	> 4 hours
MCU oxic #2	HGV-7	Air, No H_2	100	> 4 hours
Blank – Control	HGV-8	Air, No H_2	100	> 4 hours

With the long-term Test 1-2 (6 days) complete, Test 3 could utilize all seven reactors. This test evaluated a larger variety of spike materials in an oxic atmosphere of H_2-free air. The preparation of each test was very similar as the previous tests. First, all seven reactors were filled with ~95 mL of the simulant. All the spiked materials were added to the reactors filled with simulant. Table 25 shows the spikes and Table 4 shows the concentrations used. Once the spike was added the LIP was sealed and the reactors were ready for purging. The purge for each was with 15+ reactor volumes and then sealed at approximately 20 psig. The reactor head space was approximately 100 mL(reduced to ~97 mL due to the stir bar). The reactors were then heated to the target temperture of 100°C, held for more than 4 hours, and then allowed to cool overnight, with the H_2 being measured on the following day. Figure 60 shows that the reactors were heated to an average of 94°C and held for more than 4 hours. Figure 61 shows the pressures increased from about 20 to 40 psig, basically due to water vapor. As noted on the figures, the DAS wire to the pressure transducer for HGV-7 was loose and caused an intermittent signal. It was eventually found and repaired, but it left data gaps for this test. Figure 62 shows the H_2 results and as expected the spike with Admix, which contains approximately corn syrup and calcium lignin sulfonate, see Section 3.2.3, showed a much higher H_2 production. All the other spikes showed a small amounts of H_2 production that were no different than the no-spike simulant. While quantifiable, the magnitudes were not large, between 4 and 7 ppm. These data imply that grout-premix, by itself, and MCU Solvent are not significant sources of H_2 production. Figure 63 shows the HGR when the organic admix is added increased by about an order of magnitude.

Figure 60. Temperature pressure history of simulant Test 3

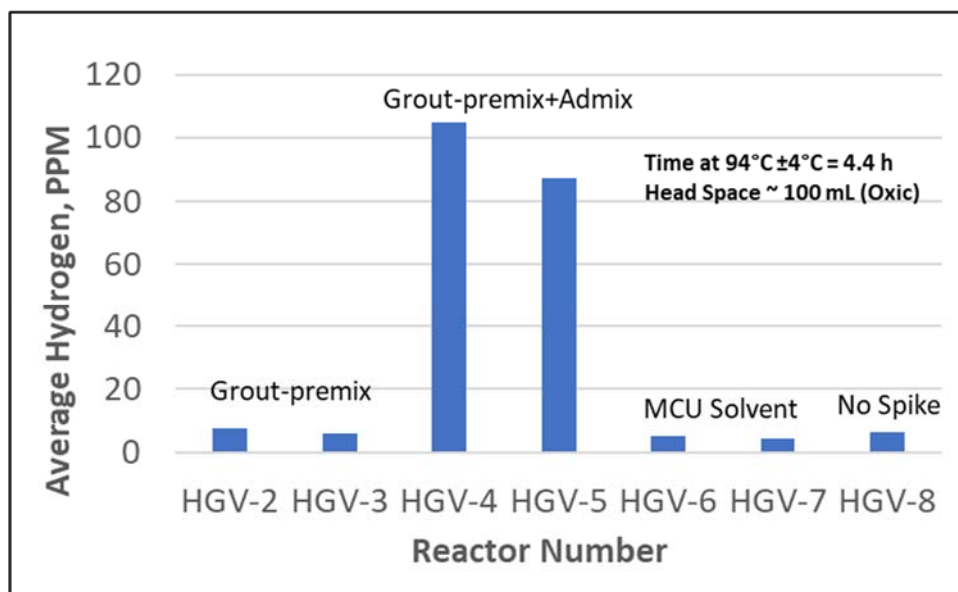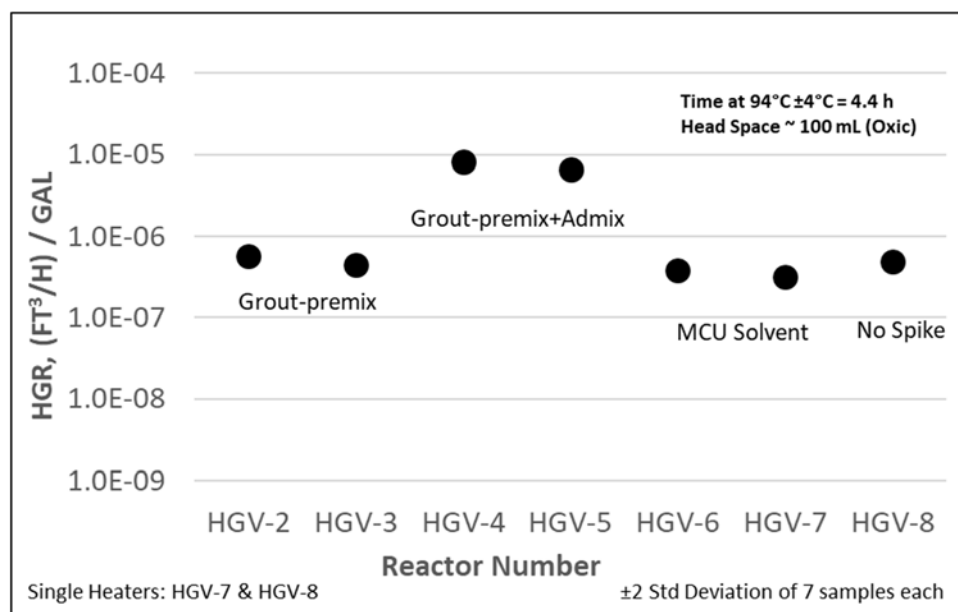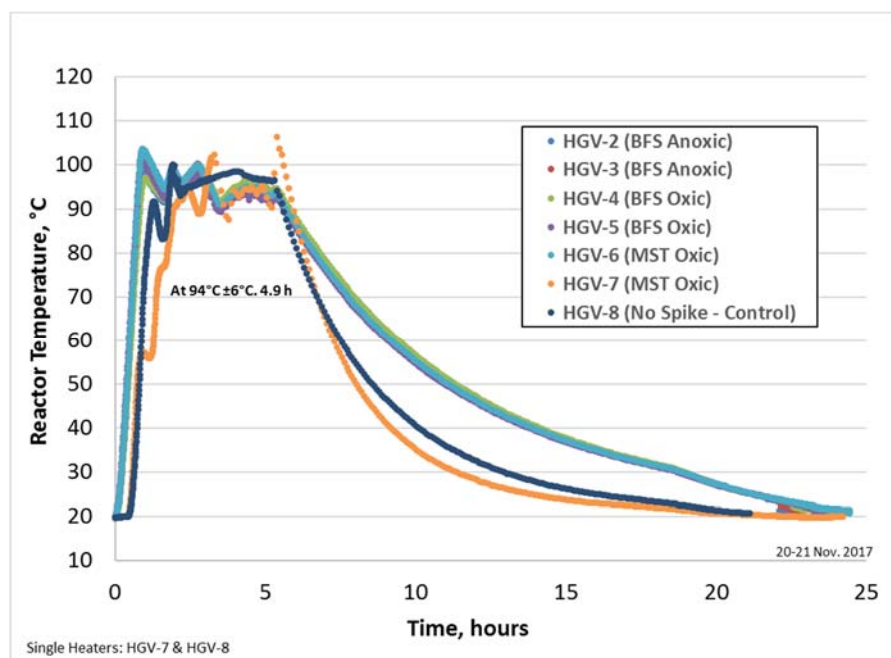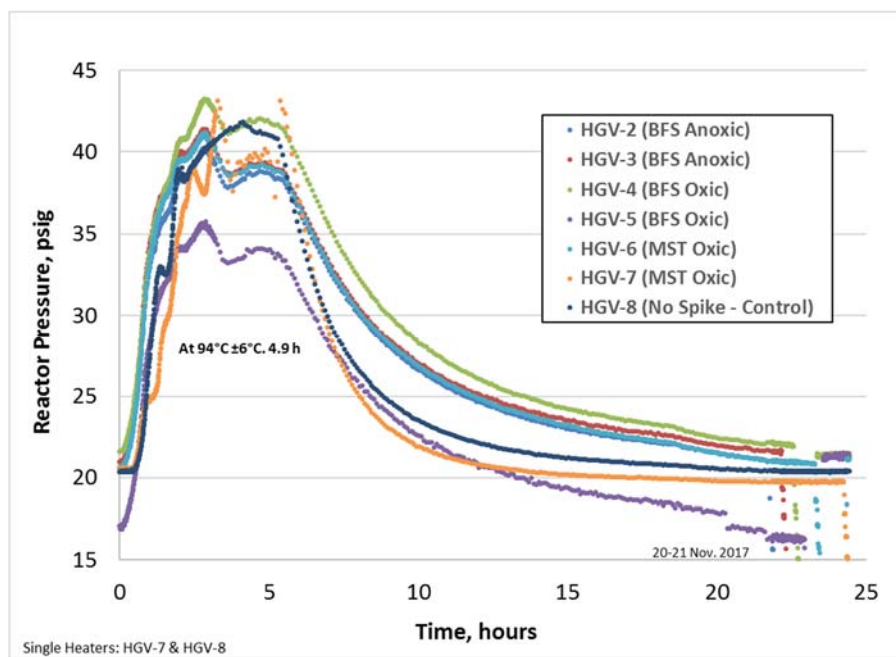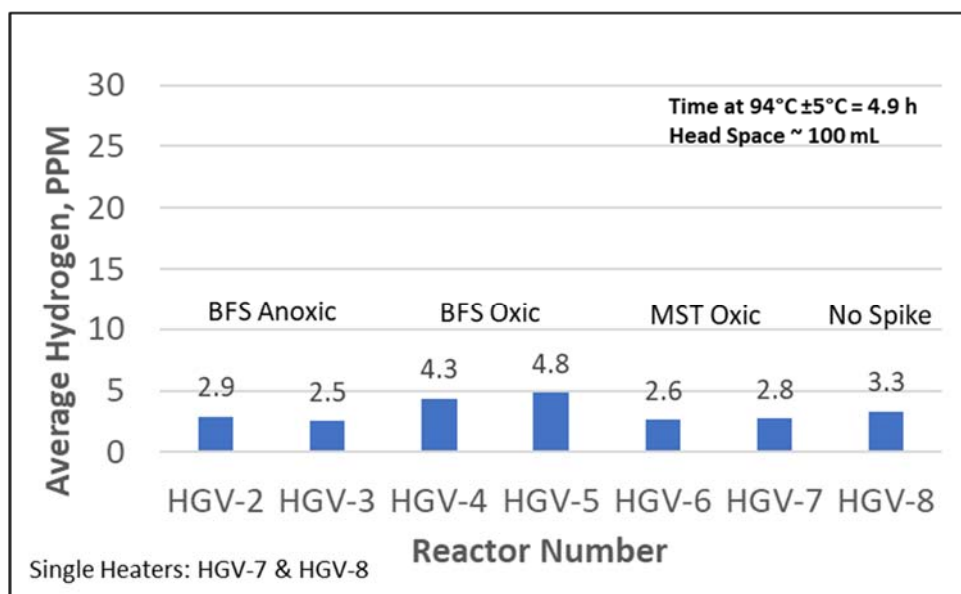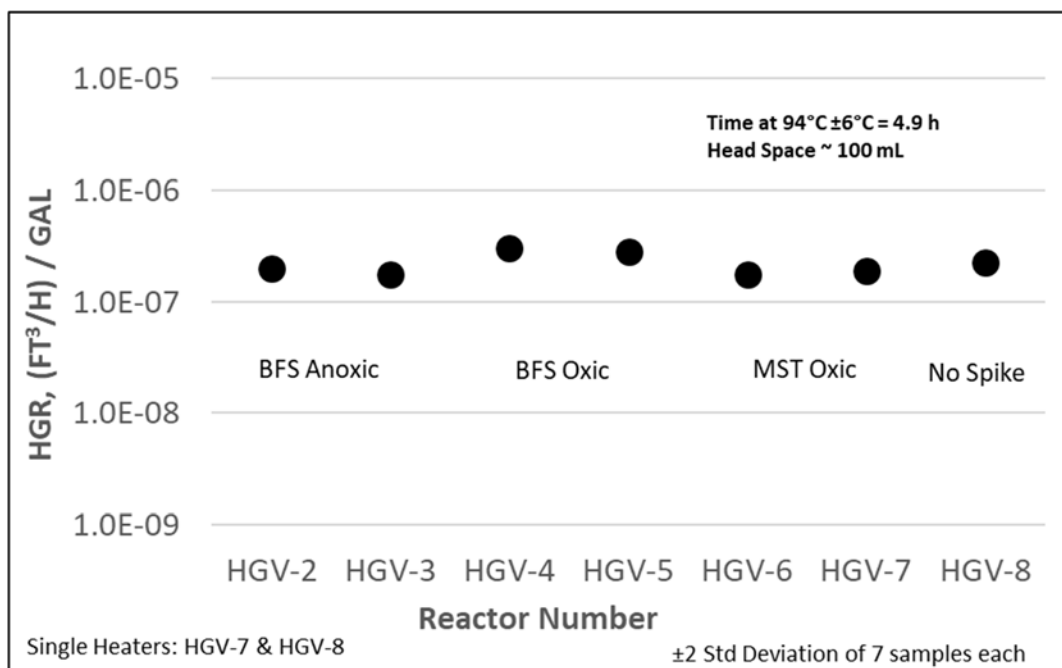**Figure 61. Pressure history of simulant Test 3**

Figure 62. H$_2$ measurements from simulant Test 3

Figure 63. HGR measurements from simulant Test 3

Test 4: Simulant test at 100°C and other conditions listed in Table 26

Table 26. Simulant Test 4

Spike Type	Reactor Used	Fill Gas	Amount of liquid, mL	Duration
BFS anoxic	HGV-2	N_2	100	> 4 hours
BFS anoxic #2	HGV-3	N_2	100	> 4 hours
BFS oxic	HGV-4	Air, No H_2	100	> 4 hours
BFS oxic #2	HGV-5	Air, No H_2	100	> 4 hours
MST oxic	HGV-6	Air, No H_2	100	> 4 hours
MST oxic #2	HGV-7	Air, No H_2	100	> 4 hours
Blank - Control	HGV-8	Air, No H_2	100	> 4 hours

This test evaluated two more spikes: BFS in both oxic and anoxic atmospheres, which is a constituent of grout-premix, and MST in an oxic atmosphere. The preparation this test was the same as the preceding test and the reader is directed to Test 3 for the method of preparing the reactors. Figure 64 shows that the reactors were heated to an average of 94°C and held for almost 5 hours. Figure 65 shows the how the pressures increased from about 20 to 40 psig, basically due to water vapor. Figure 66 shows the H_2 results and they are no different than the simulant without any spike material. All the H_2 values range from 2 and 5 ppm. Furthermore, there are no significant difference between the oxic and anoxic atmospheres. Figure 67 shows the HGR for all the reactors to be similar, on the order of about 10^{-7} (ft^3/h)/gal.
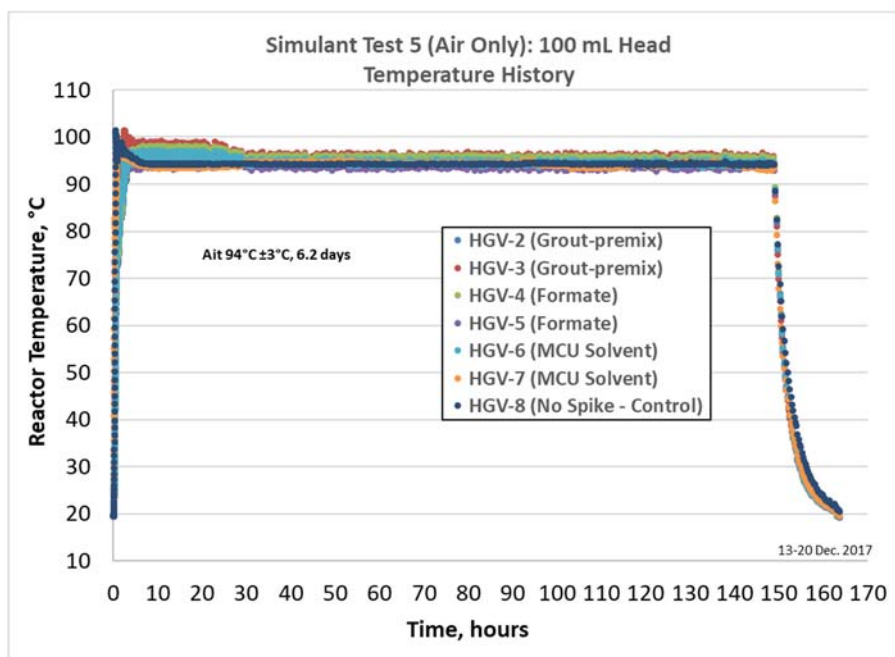

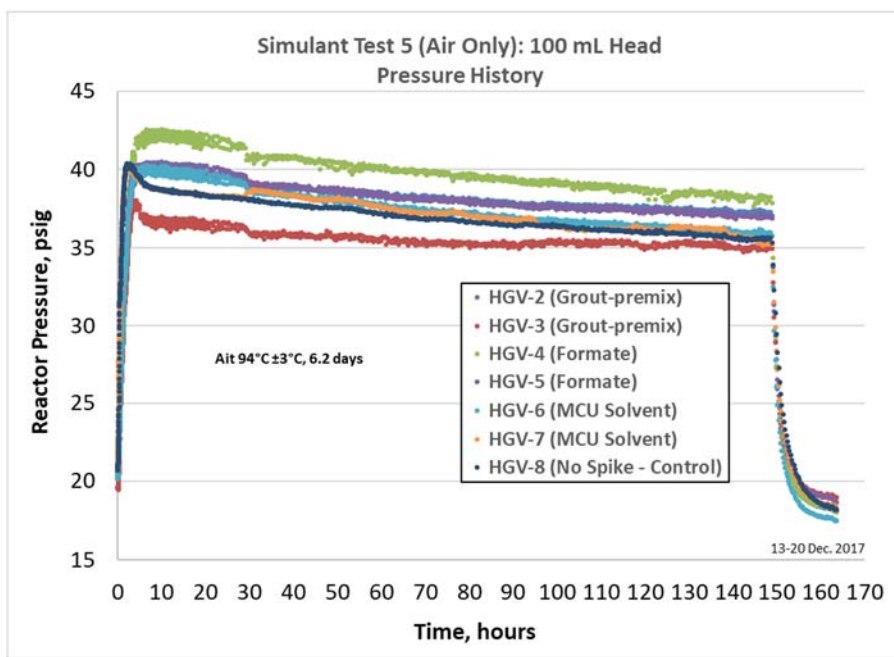**Figure 64. Temperature history of simulant Test 4**

Figure 65. Pressure history of simulant Test 4

Figure 66. H₂ measurements from simulant Test 4

Figure 67. HGR measurements from simulant Test 4

Test 5: Simulant test at 100°C and other conditions listed in Table 27

Table 27. Simulant Test 5

Spike Type	Reactor Used	Fill Gas	Amount of liquid, mL	Duration
Grout-premix	HGV-2	Air, No H_2	100	> 6 days
Grout-premix #2	HGV-3	Air, No H_2	100	> 6 days
Formate	HGV-4	Air, No H_2	100	> 6 days
Formate #2	HGV-5	Air, No H_2	100	> 6 days
MCU Solvent	HGV-6	Air, No H_2	100	> 6 days
MCU Solvent #2	HGV-7	Air, No H_2	100	> 6 days
Blank - Control	HGV-8	Air, No H_2	100	> 6 days

The previous four-hours test had a significant heat up period and cool down period, relative to the heating period; therefore, this last test was performed over a 6-day period to reduce the impact to the measured data from the start up and cooling periods. However, besides the longer time of heating, the preparations to fill, spike, and heat the reactors were the same as previous test. The reader is referred to previous sections to understand those activities.

Figure 68 shows that the reactors we heated to an average of 94°C and held for more than 148 hours (~6 days). Figure 69 shows the how the pressures increased from about 20 to 40 psig, basically due to water vapor. Figure 70 shows the H_2 results and while all the reactor showed H_2 concentration about an order of magnitude larger than the 4-hour tests, they, once again, appear to be no different than the simulant without any spike material. All the H_2 values were small range from 25 and 50 ppm. Figure 71 shows the HGR for all the reactors to be similar, on the order of about 5×10^{-8} (ft^3/h)/gal.

Figure 68. Temperature history of simulant Test 5

Figure 69. Pressure history of simulant Test 5
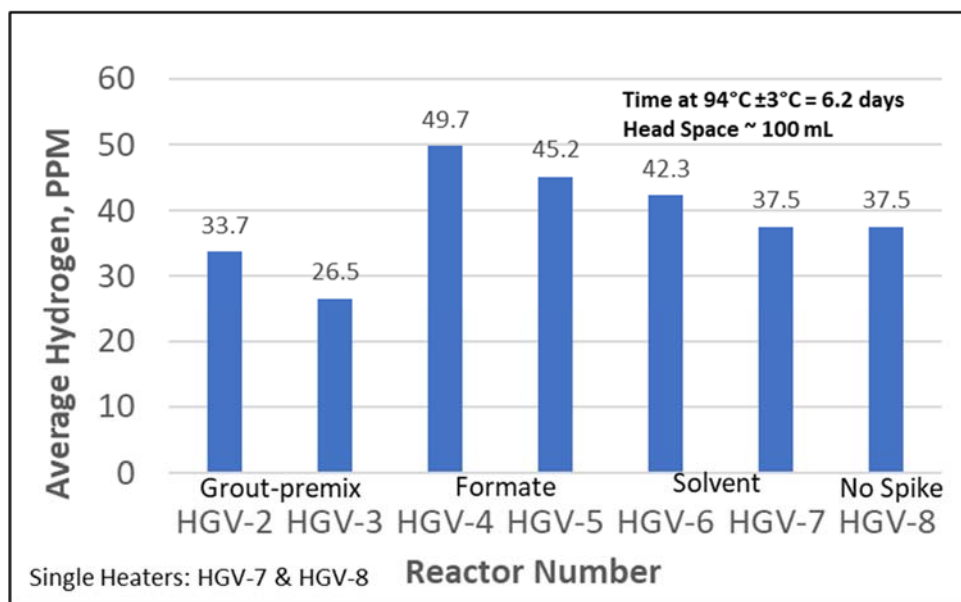
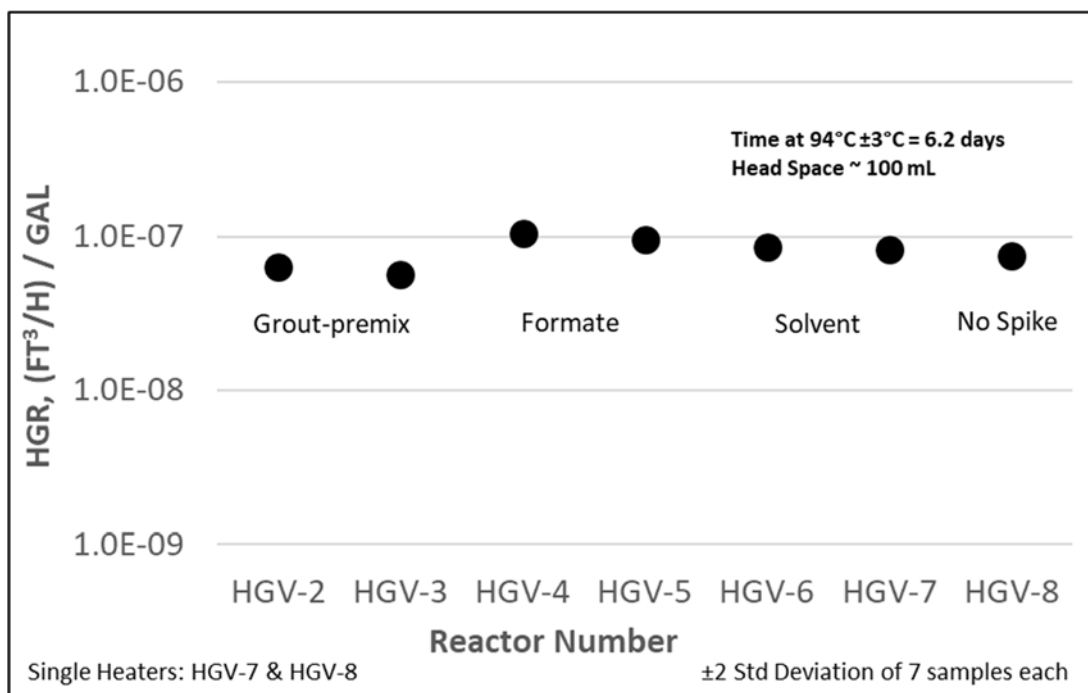**Figure 70. H₂ measurements from simulant Test 5**

Figure 71. HGR measurements from simulant Test 5

Appendix H: Tank 50 Individual Test Results

Radioactive testing included five planned campaigns, but after evaluating the safety documentation it was necessary to include an initial test with an anoxic head space to quantify the H_2 production to demonstrate that the lower flammability level (LFL) would not be exceeded. As testing progressed, a final test was added to repeat some important tests over a longer period then the 16 hours that most test utilized. This is documented in the revised run plan [7.24]. This appendix discusses each of the tests in detail.

The following data for each test will be presented by the measurements of: Temperature History, Pressure History, and the H_2, which was obtained during the gas sampling of each reactor after it returned to room temperature. This information, along with reactor specifics, is used to create the last graph, which shows the result of a calculation of HGR. That calculation is adjusted to a pressure of 1 atmosphere (14.7 psia) and a temperature of 25°C. That is, for the HGR calculation, the sampling initial pressure, which was usually close to 20 psig, and temperature, which was usually between, 22°C to 28°C, were adjusted so all the graphical data are adjusted to 1 atm and 25°C. The equation used for HGR was:

[[(Head Space Volume, ft³) • A • H_2 Measured, ppm / 1000000] / (Test Time, hours)] / Volume Liquid, gal

Where A =

[Pinitial sample / Pstandard] [Tstandard/Tsampling] =

[(Initial Sample Head Pressure, psig + 14.7 psia) / 14.7 psia] [298 K / (T°C at sampling+273 K)]

With Pstandard = 14.7 psia and Tstandard = 25°C

Test 1: Tank 50 waste test at 120°C and other conditions listed in Table 28

Table 28. First Tank 50 Radioactive Test

Spike Type	Reactor Used	Fill Gas	Temperature °C	Amount of liquid, mL	Duration h
None, Control	HGV-2	N_2	120	100	>16
BFS	HGV-3	N_2	120	100	>16
Grout-premix	HGV-4	N_2	120	100	>16

Test 1 and Test 2 were the same except that Test 1 used nitrogen as the head space gas to quantify the H_2 produce with an anoxic atmosphere to demonstrate that the lower flammability level (LFL) would be exceeded. The preparation of the next five test was the same, so it will only be explained here.

With three clean 195-mL reactors they were filled with enough Tank 50 waste to produce a 100-mL head space (reduced to 97 mL due to the stir bar). After filling each reactor, one reactor received BFS solids, one grout-premix solids, and the last reactor received no spike, to be control. Then all three were purged with 15+ reactor volumes of H_2-free nitrogen and sealed at approximately 20 psig of pressure. The reactors installed on the stirrer/hotplate and internal Teflon-coated strirrer was activated. It would stir the entire time the reactors were heated. The reactors were insulated and heated to the target temperture of 100°C and held for more than 16 hours using temperature controller for overnight operation. After 16+ hours on the following day the reactors were removed from the stirrer/hotplate an allowed to cool until the pressure dropped to the initial pressure of approximately 20 psig. At this point the reactors were ready to sample for H_2.

Figure 72 shows that the reactors were heated to an average of 115°C and held for more than 17 hours. Figure 73 shows the how the pressures increased from about 20 to 50 psig, basically due to water vapor. Figure 74 shows the H_2 results show a clear trend with the control sample having the lowest H_2 production at about 70 ppm, BGS significantly higher, about double the production at 130 ppm, and then grout-premix slight higher still at 160 ppm. Note, the control reactor, HGV-2, Figure 73, show a slight drop in pressure near the end of the 17 hours, which may have an impact on that result, but the actual impact is not known. The results from the three reactors imply the spikes have an effect. The highest H_2 concentration of 160 ppm was more than an order of magnitude less than the LFL of 10,000 ppm. This meant the rest of the tests could proceed using an air atmosphere. Figure 75 shows the HGR to be about 10^{-6} (ft^3/h)/gal.
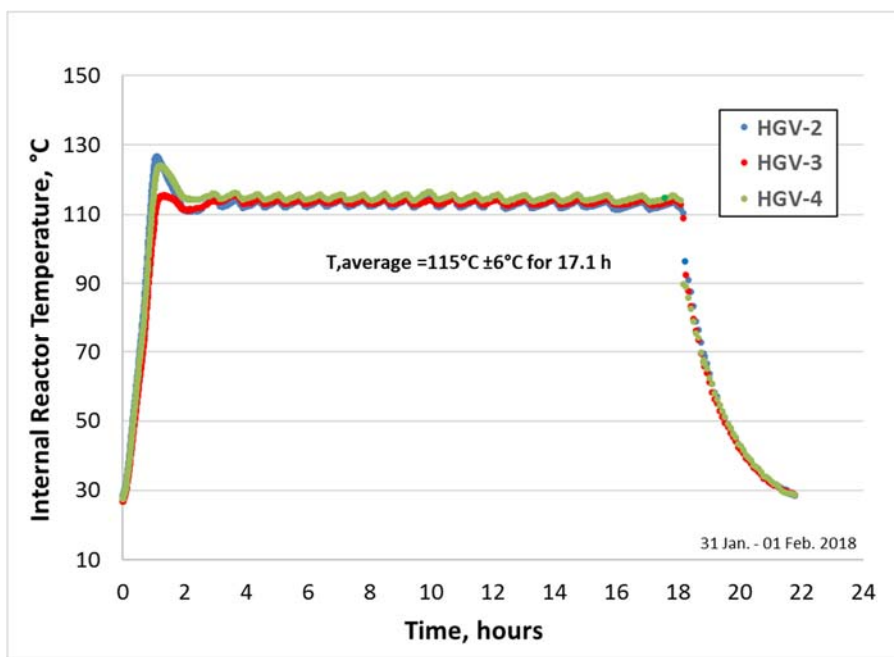
Figure 72. Temperature history of radioactive-waste Test 1
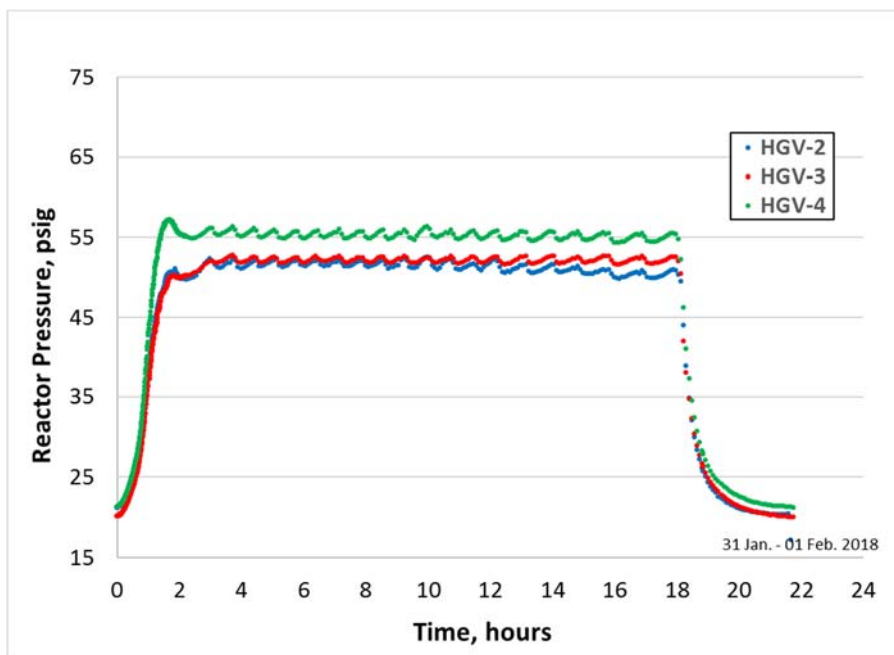

Figure 73. Pressure history of radioactive-waste Test 1
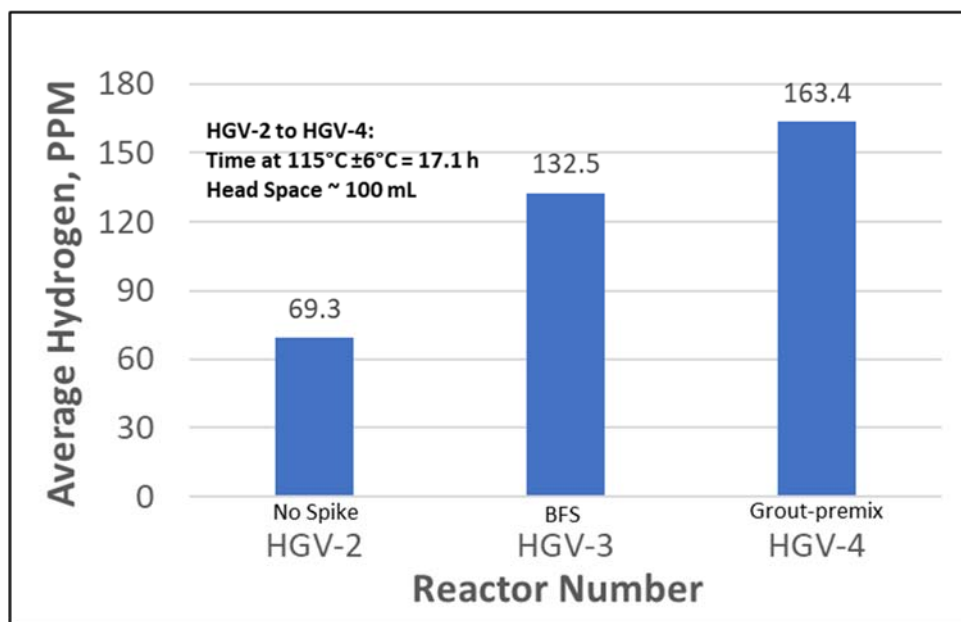
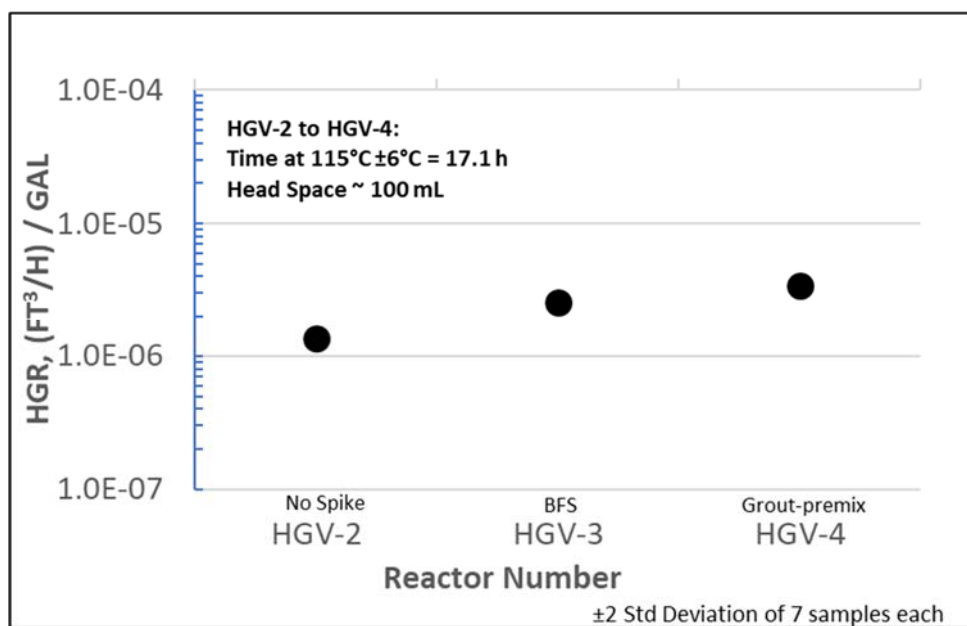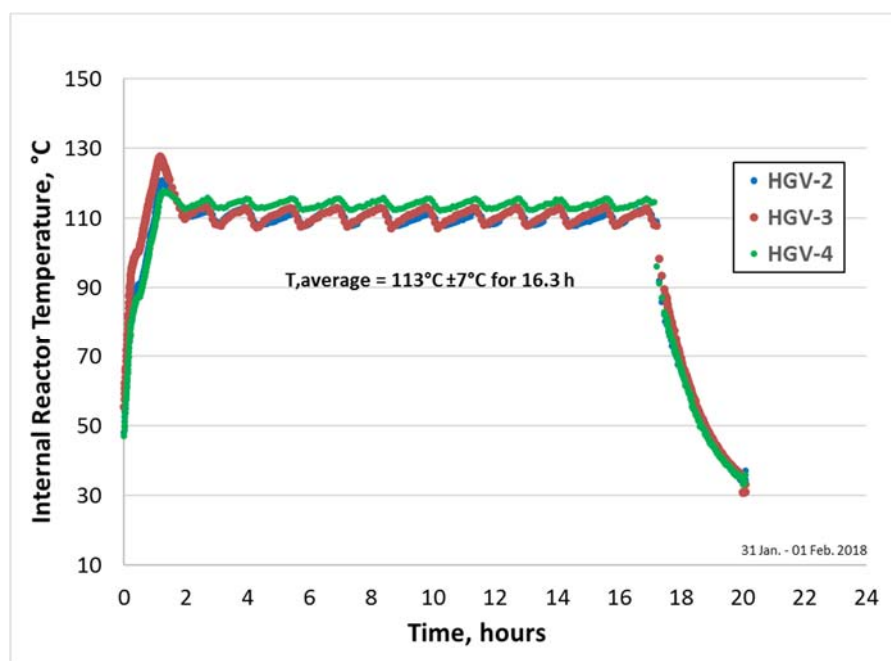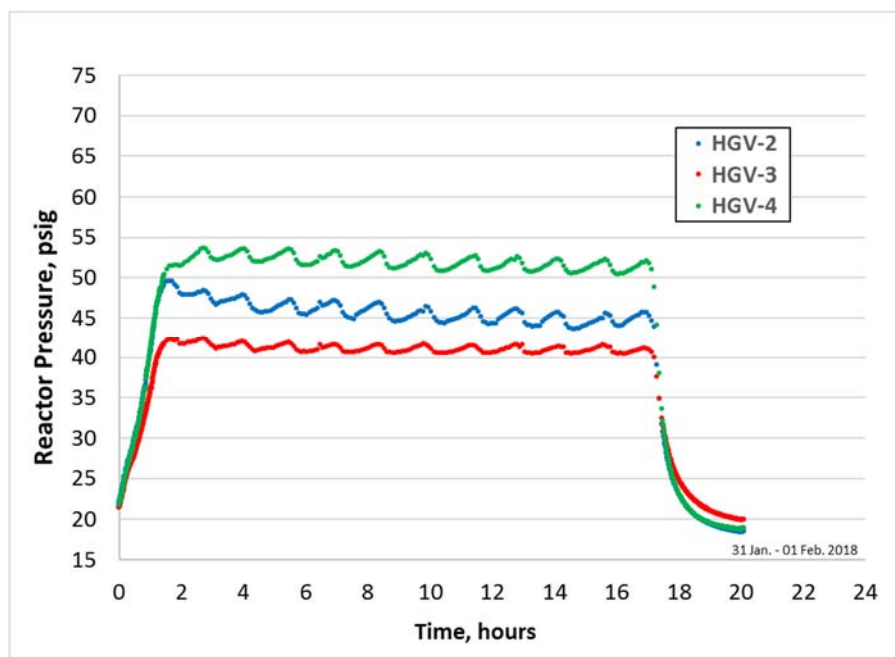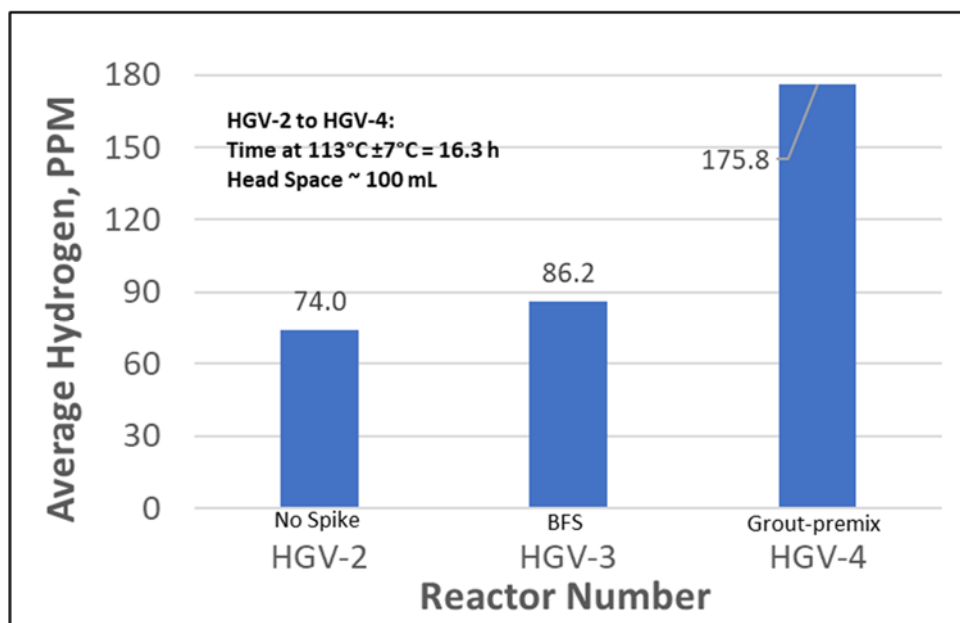**Figure 74. H₂ measurements from radioactive-waste Test 1**

Figure 75. HGR measurements from radioactive-waste Test 1

Test 2: Tank 50 waste test at 120°C and other conditions listed in Table 29

Table 29. Second Tank 50 Radioactive Test

Spike Type	Reactor Used	Fill Gas	Temperature °C	Amount of liquid, mL	Duration h
None, Control	HGV-2	Air, No H_2	120	100	>16
BFS	HGV-3	Air, No H_2	120	100	>16
Grout-premix	HGV-4	Air, No H_2	120	100	>16

Test 2 is the first radioactive test to use an oxic atmosphere of H_2-free air. It was the same as Test 1, except for the change in gas. As stated in Test 1, see Test 1 for the preparation of the reactors.

Figure 76 shows that the reactors were heated to an average of 113°C and held for more than 16 hours. Figure 77 shows the how the pressures increased from about 20 to 50 psig, basically due to water vapor. Figure 78 shows the H_2 results showed the same trend as Test 1; that is, a clear trend with the control sample having the lowest H_2 production at about 74 ppm, BGS slightly higher at 86 ppm, and then grout-premix significantly higher at 176 ppm. The difference between Test 1 and 2 is how close the BGS result is to the non-spiked result. Figure 79 still shows the HGR at about 10^{-6} (ft^3/h)/gal.

Figure 76. Temperature history of radioactive-waste Test 2

Figure 77. Pressure history of radioactive-waste Test 2

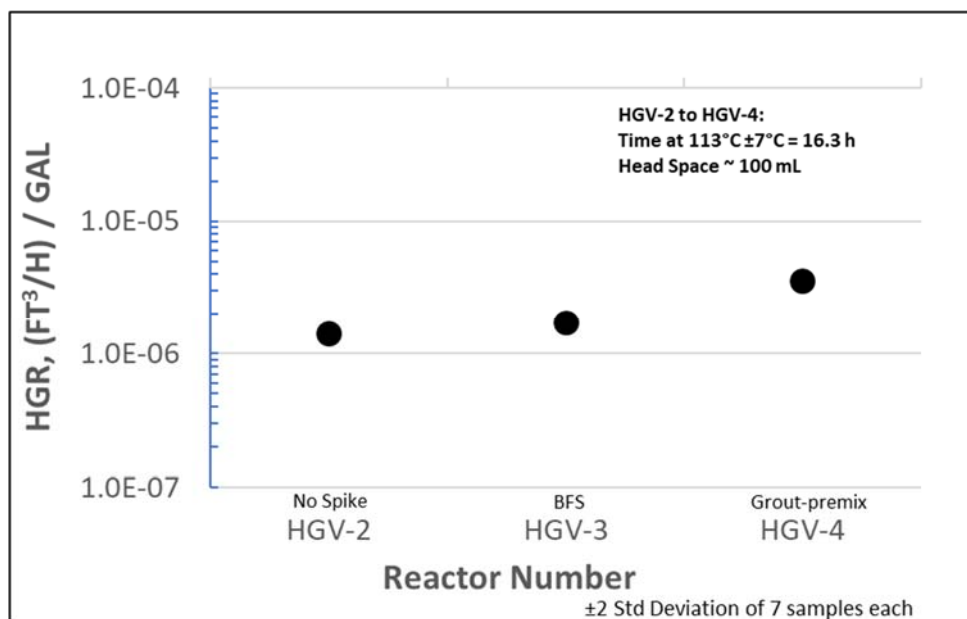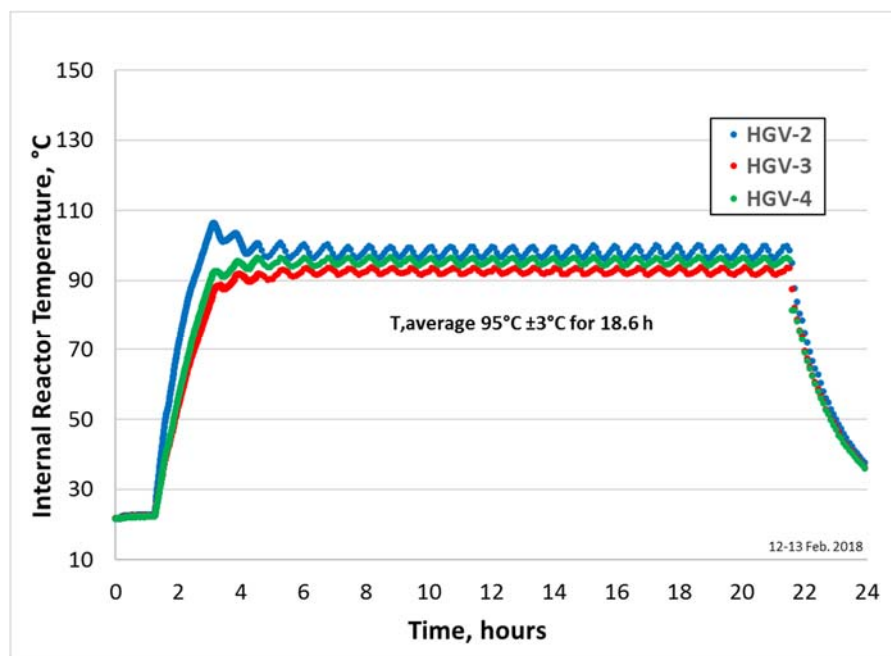**Figure 78. H₂ measurements from radioactive-waste Test 2**

Figure 79. HGR measurements from radioactive-waste Test 2

Test 3: Tank 50 waste test at 100°C and other conditions listed in Table 30

Table 30. Third Tank 50 Radioactive Test

Spike Type	Reactor Used	Fill Gas	Temperature °C	Amount of liquid, mL	Duration h
None, Control	HGV-2	Air, No H_2	100	100	>16
BFS	HGV-3	Air, No H_2	100	100	>16
Grout-premix	HGV-4	Air, No H_2	100	100	>16

Now from Test 2 to Test 5 the temperature is successively lower, but everything else remains the same. Figure 80 shows that the reactors were heated to an average of 95°C and held for more than 18 hours. Figure 81 shows the how the pressures increased from about 20 to 40 psig, basically due to water vapor. Figure 82 shows the H_2 results displayed the same trend as Test 1, that is, a clear trend with the control sample having the lowest H_2 production at about 16 ppm, BGS significantly higher, with double the concentration at 32 ppm, and then grout-premix slightly higher still at 45 ppm. The significant difference is from the reduced temperature. By dropping the temperature 20°C H_2 concentration dropped by a factor of ~4. Figure 83 shows the HGR approaching 10^{-7} (ft^3/h)/gal.

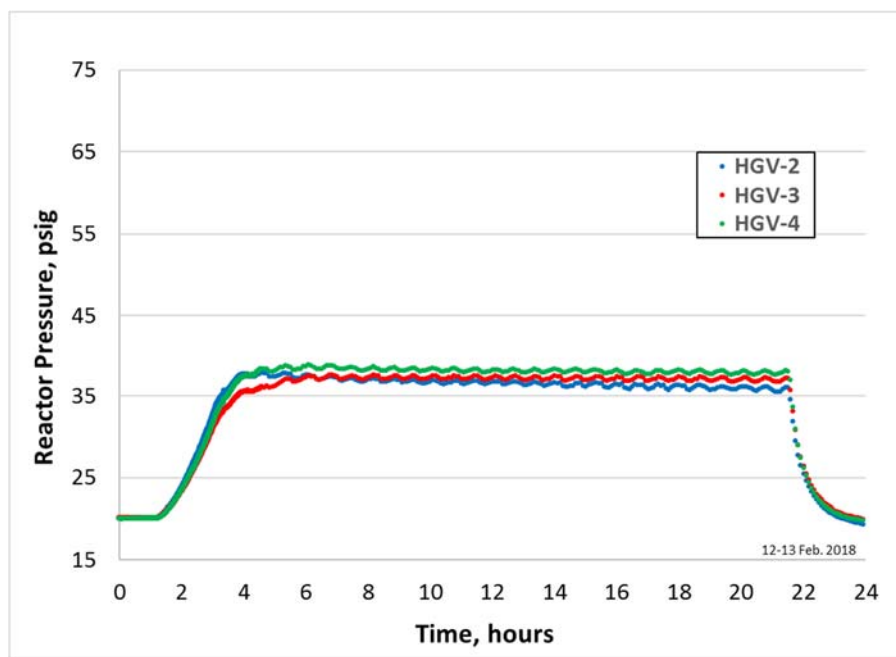**Figure 80. Temperature history of radioactive-waste Test 3**

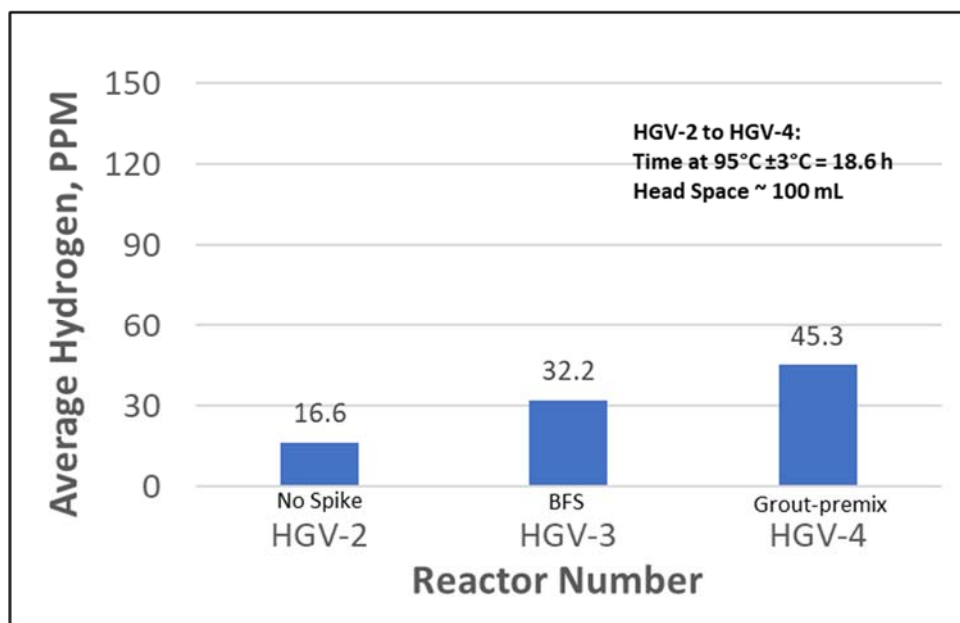**Figure 81. Pressure history of radioactive-waste Test 3**
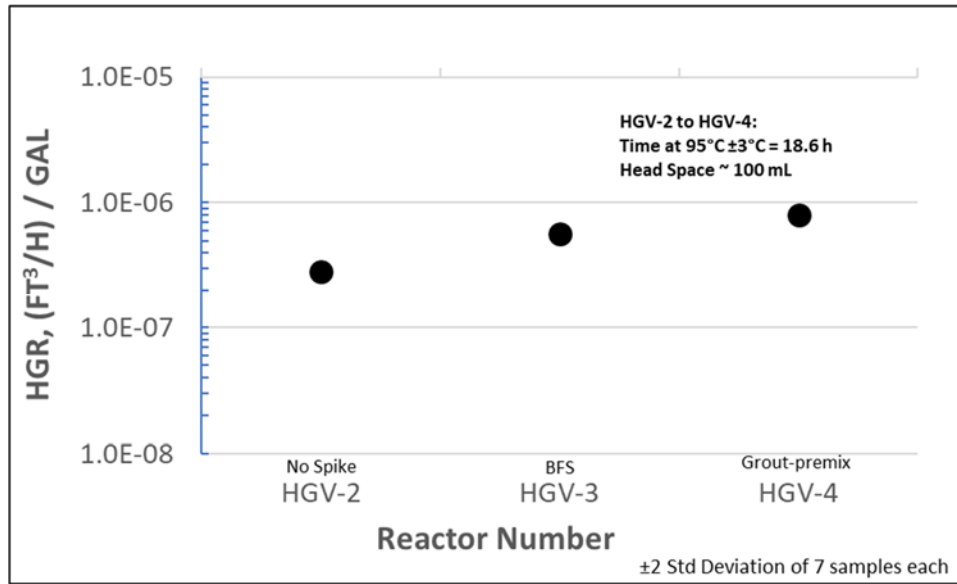

Figure 82. H₂ measurements from radioactive-waste Test 3

Figure 83. HGR rate measurements from radioactive-waste Test 3

Test 4: Tank 50 waste test at 75•C and other conditions listed in Table 31

Table 31. Fourth Tank 50 Radioactive Test

Spike Type	Reactor Used	Fill Gas	Temperature °C	Amount of liquid, mL	Duration h
None, Control	HGV-2	Air, No H_2	75	100	>16
BFS	HGV-3	Air, No H_2	75	100	>16
Grout-premix	HGV-4	Air, No H_2	75	100	>16

Figure 84 shows that the reactors were heated to an average of 72°C and held for more than 20 hours. Figure 85 shows the how the pressures increased from about 20 to 30 psig, basically due to water vapor. Figure 86 shows the H_2 results with the control sample having the lowest H_2 production at about 1.4 ppm, which is barely above the detectable limit of 1 ppm, BGS significantly higher, at four times the concentration at 6 ppm, and then grout-premix slightly higher still at 7 ppm. Once again, the significant difference is from the reduced temperature. By dropping the temperature another 20°C H_2 concentration dropped by almost an order of magnitude. Figure 87 shows the HGR for non-spike waste is approaching 10^{-9} (ft^3/h)/gal.
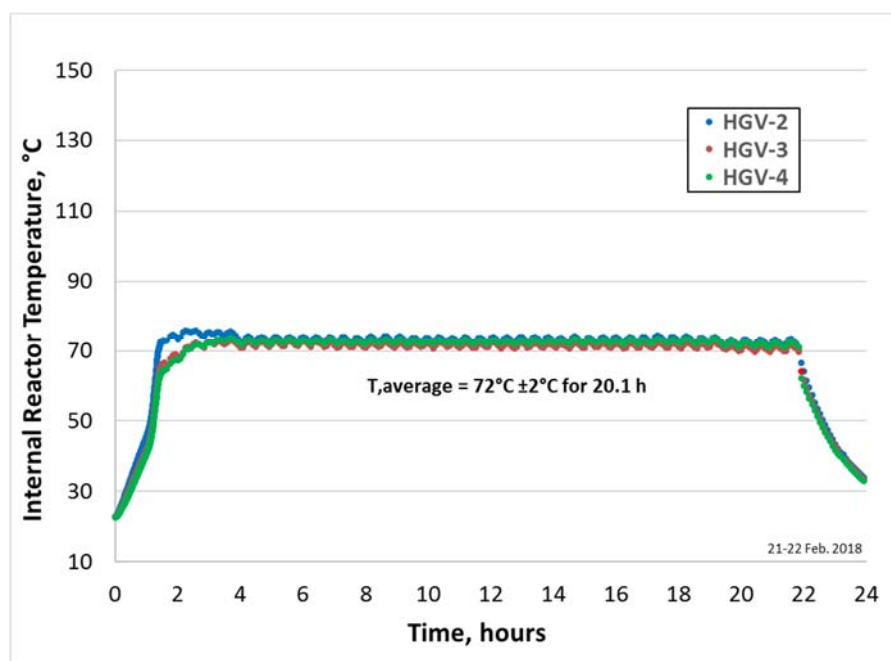

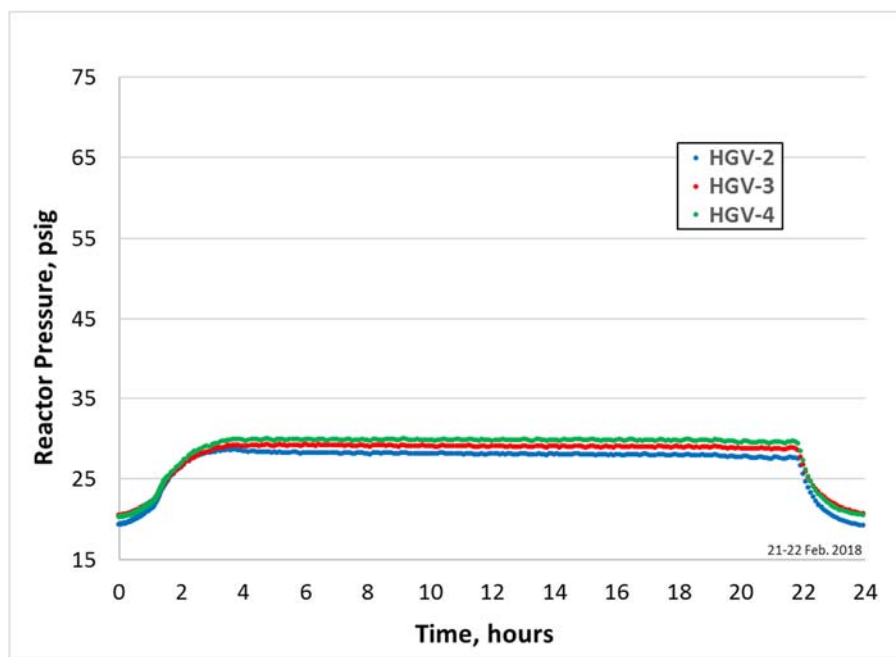**Figure 84. Temperature history of radioactive-waste Test 4**

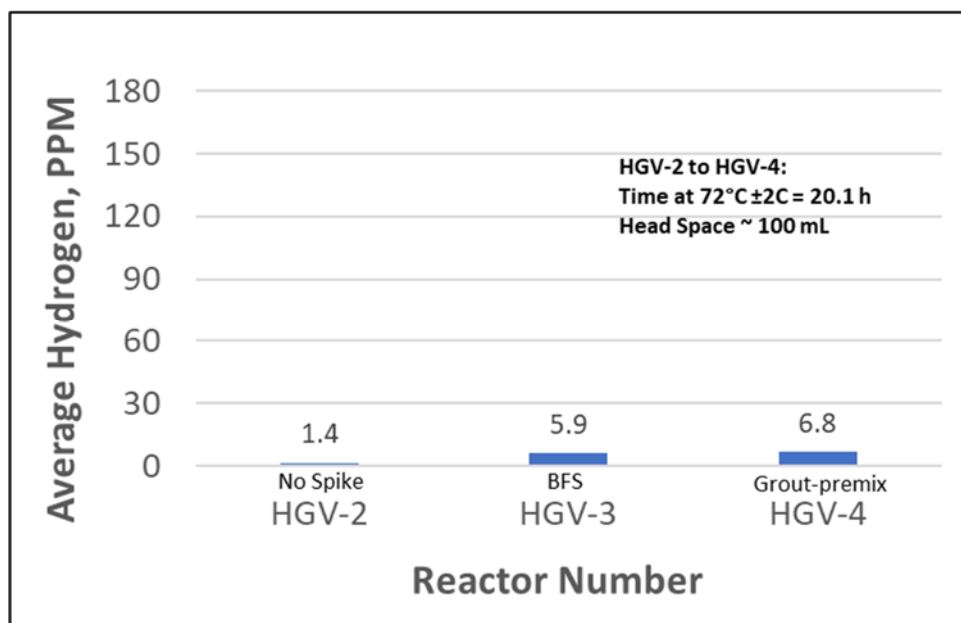**Figure 85. Pressure history of radioactive-waste Test 4**

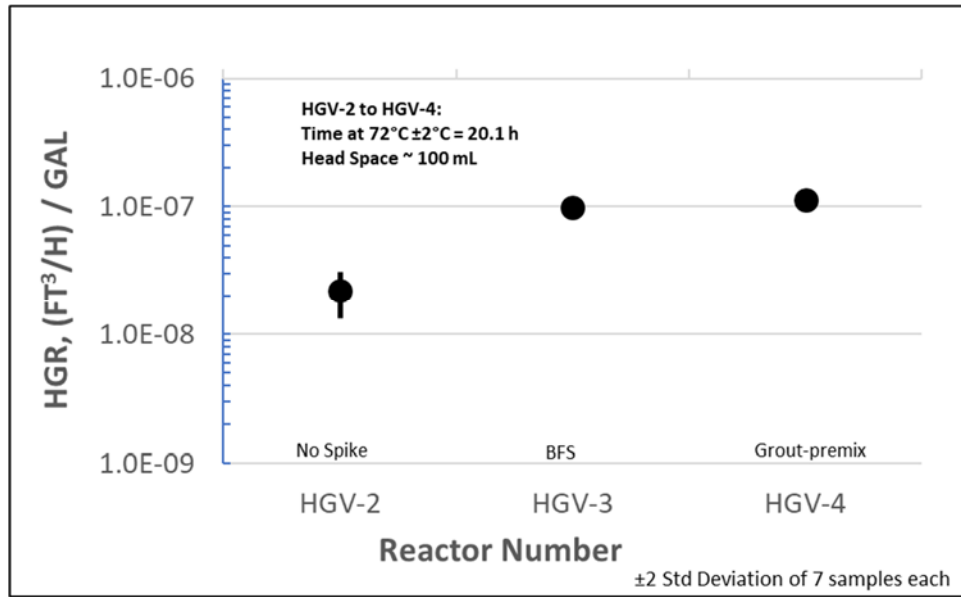**Figure 86. H₂ measurements from radioactive-waste Test 4**

Figure 87. HGR measurements from radioactive-waste Test 4

Test 5: Tank 50 waste test at 50•C and other conditions listed in Table 32

Table 32. Fifth Tank 50 Radioactive Test

Spike Type	Reactor Used	Fill Gas	Temperature °C	Amount of liquid, mL	Duration h
None, Control	HGV-2	Air, No H_2	50	100	>16
BFS	HGV-3	Air, No H_2	50	100	>16
Grout-premix	HGV-4	Air, No H_2	50	100	>16

This is the lowest temperature 16-hour test and completes the set of 3-reactor tests. Figure 88 shows that the reactors we heated to an average of 49°C and held for 21 hours. Figure 89 shows how the pressures increased from about 20 to 25 psig, basically due to water vapor. A drift downwards of HGV-2 is observed and afterwards one of the seals had to be replaced. However, by the time the reactor was sampled still had 85% of its original pressure, so the measurements were still deemed accurate. Figure 90 shows the H_2 results and at this reduced temperature the three reactors are almost indistinguishable. Both reactors with spike waste are barely above what can be detected by the GC and the non-spiked waste showed no H_2 after 21 hours of heating. It is probably fair to say that at 50°C and below the effect of thermolysis on H_2 production is insignificant. Figure 91 shows the HGR for spike waste approaching 10^{-9} (ft^3/h)/gal.
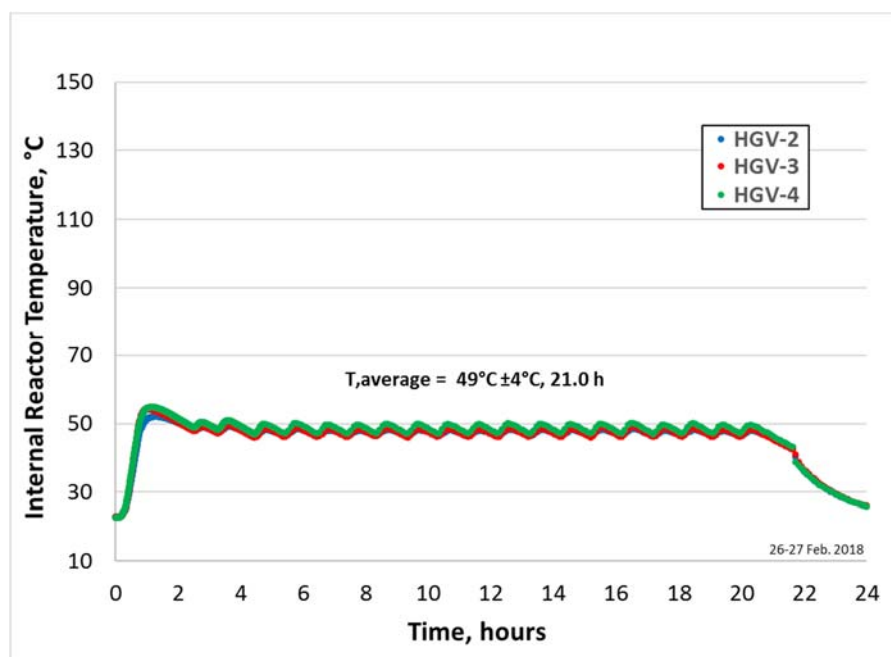

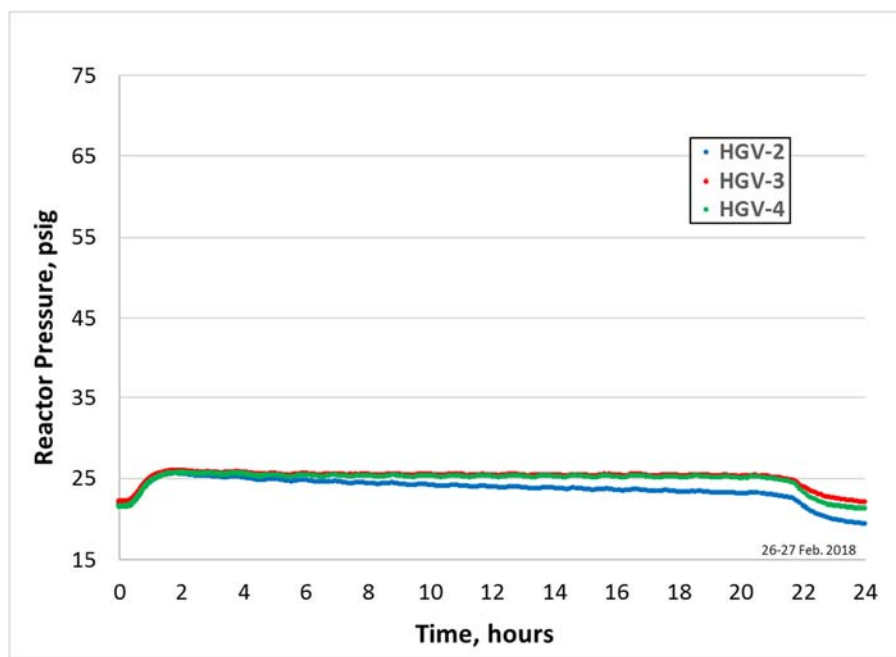**Figure 88. Temperature history of radioactive-waste Test 5**

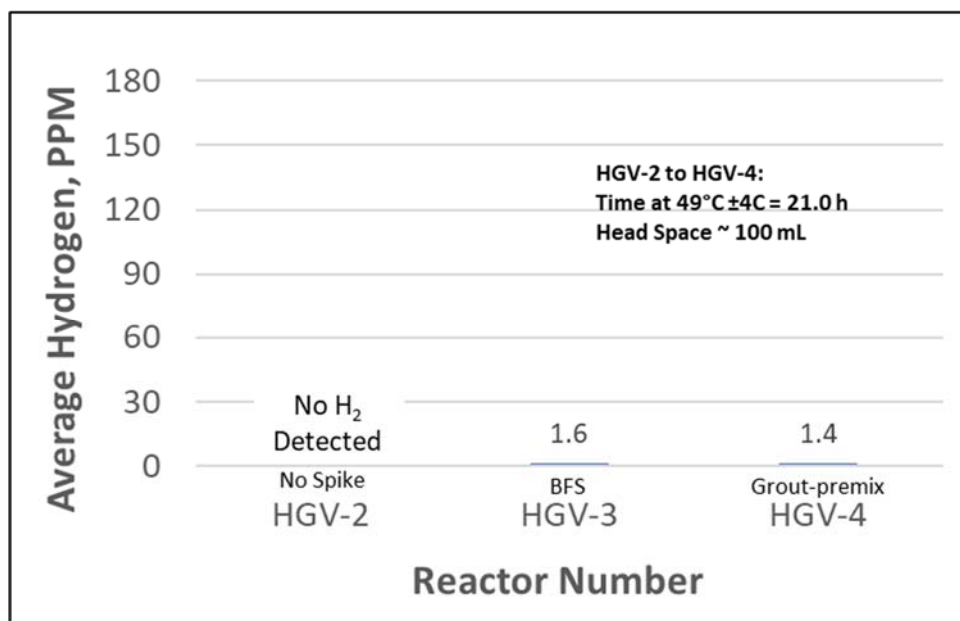**Figure 89. Pressure history of radioactive-waste Test 5**

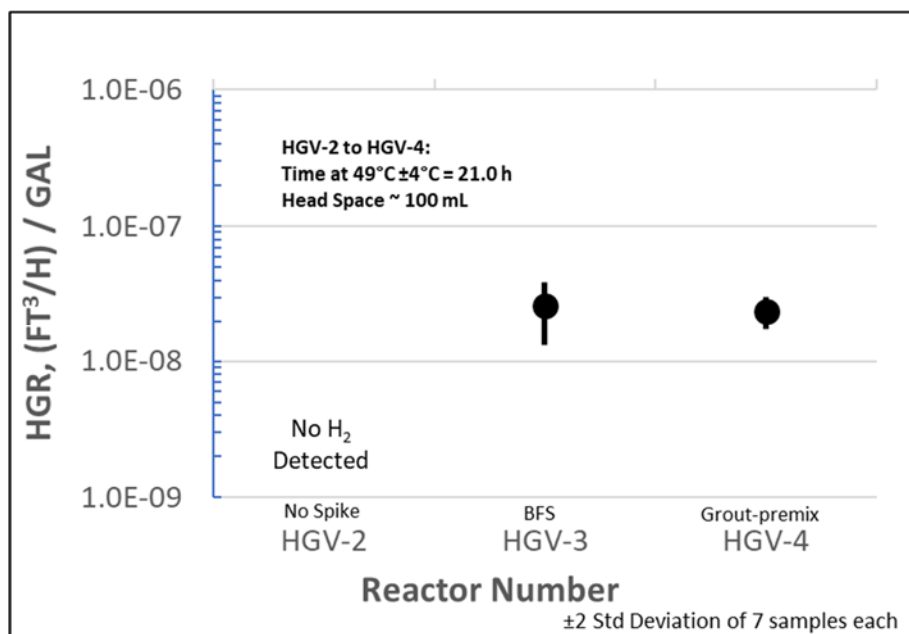**Figure 90. H$_2$ measurements from radioactive-waste Test 5**

Figure 91. HGR measurements from radioactive-waste Test 5

Test 6: Tank 50 waste test at 32°C and other conditions listed in Table 33

Table 33. Sixth Tank 50 Radioactive Test

Spike Type	Reactor Used	Fill Gas	Temperature °C	Amount of liquid mL	Duration days
None, Control	HGV-5	Air, No H_2	32	180	>26
None, Control	HGV-6	Air, No H_2	32	180	>26

Test 6 was the longest-term test at 26 days where the effect of radiolysis was to be demonstrated. Two reactors were set aside with Tank 50 waste and no spikes. The reactors were filled with enough waste to allow only a 20-mL head space to increase the sensitivity of measurement. The temperature was not really at room temperature, but maintained slightly above at 32°C so it could be steadier than real room temperature that can fluctuate 10°C, or more, over the 26 days of the test.

Figure 92 shows that the reactors when heated to an average of 32°C and held for 21 hours. Figure 93 shows the how the pressures increased from about 20 to 22 psig, basically due to water vapor, Figure 94 shows those pressures after normalized with the starting pressure. Here the normalized pressure is important because on the 13th day of testing one of the reactors, HGV-5 was sampled and then resealed. The sampling episode caused the reactor pressure to drop from about 20 psig to 6.4 psig. By normalizing to the new starting pressure, the pressure held. There is a change during the last few days of test that is unexplained; for some reason, the stirrer/hotplate jumped a couple of degrees. Figure 95 shows the H_2 results that are measurable but small values. Figure 96 shows the HGR for no-spike waste approaching 10^{-9} (ft^3/h)/gal.

Over 26-day period at 32°C, Tank 50 Waste averaged HGR of 1.32 x 10^{-9} (ft^3/h)/gal ± 0.14 x 10^{-9} (ft^3/h)/gal, which is consider radiolytic due to the low temperature.

As shown on Figure 96, this HGR result is significantly below the estimated SRR WCS radiolytic values of 3.09 x 10^{-9} (ft^3/h)/gal for Supernatant and 5.08 x 10^{-9} (ft^3/h)/gal for slurry (see Appendix I), which means the estimates are conservative.

This HGR result matches, within uncertainty, the Monte Carlo n-Particle Code estimate of radiolytic rate of 5.1 x 10^{-10} (ft^3/h)/gal from a 180-mL batch of waste [7.14].
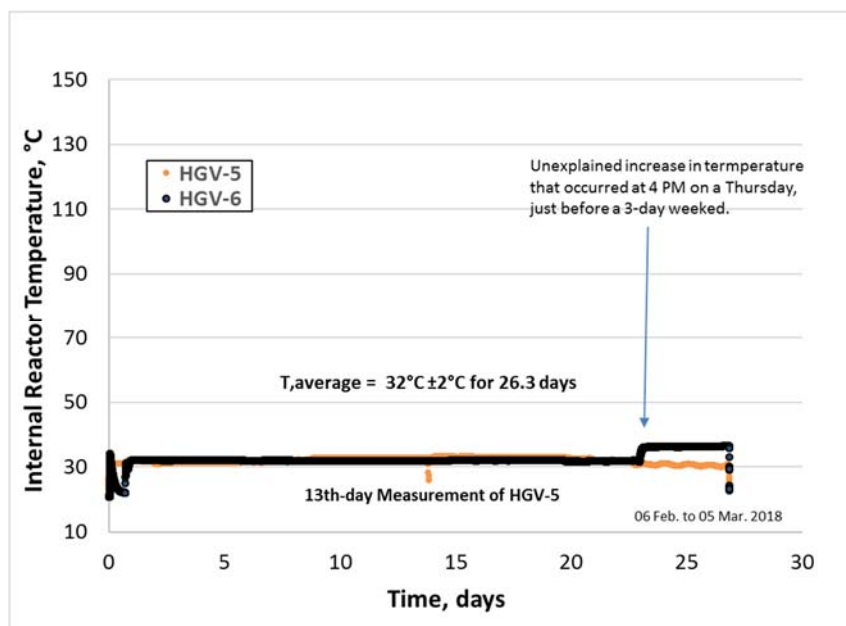
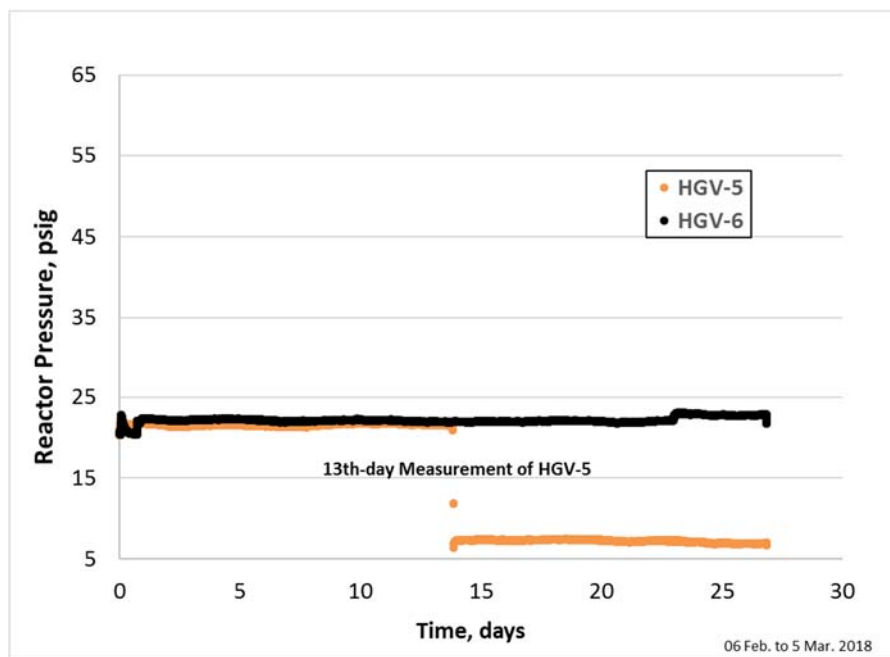**Figure 92. Temperature history of radioactive-waste Test 6**

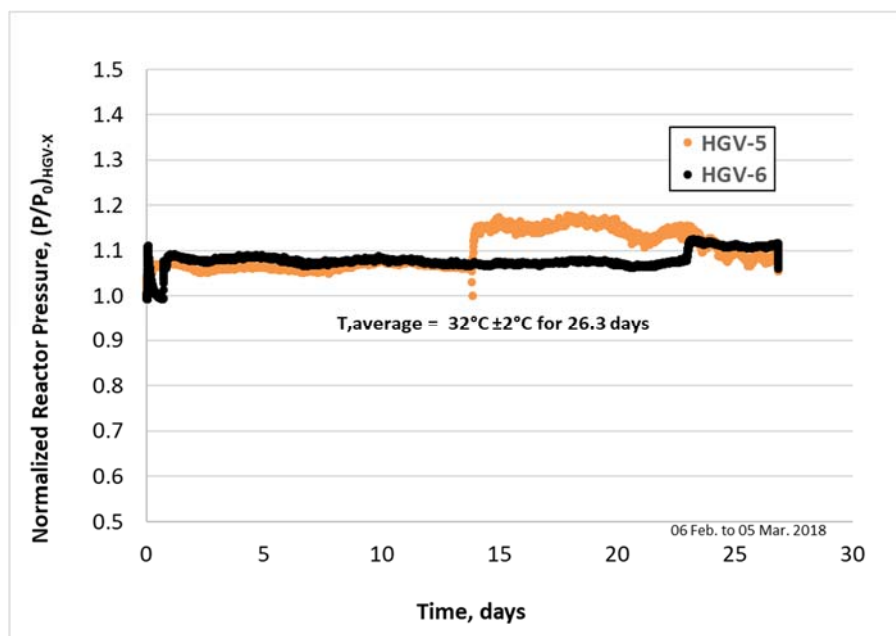**Figure 93. Pressure history of radioactive-waste Test 6**

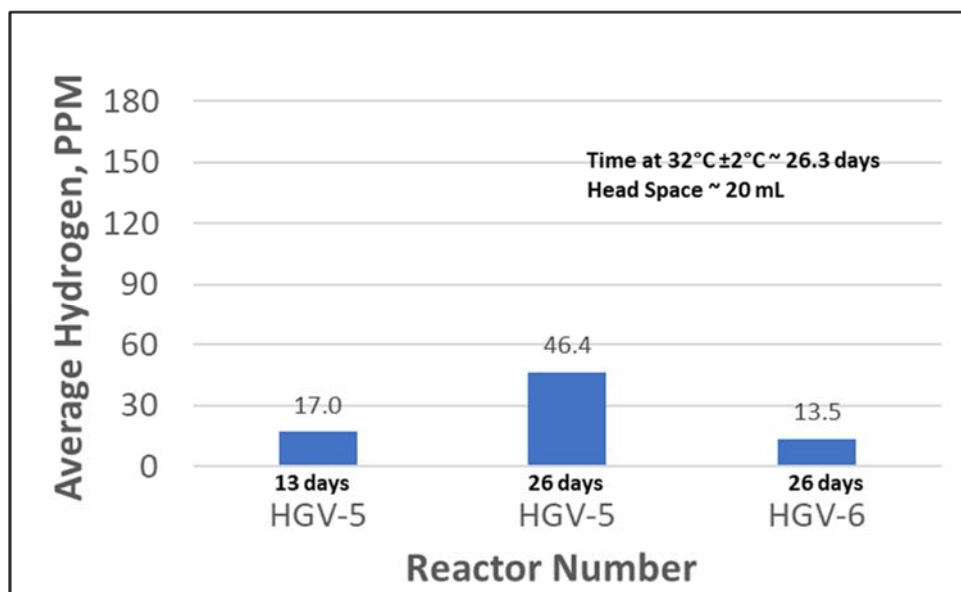**Figure 94. Pressure history of radioactive-waste Test 6, normalized to initial pressure**

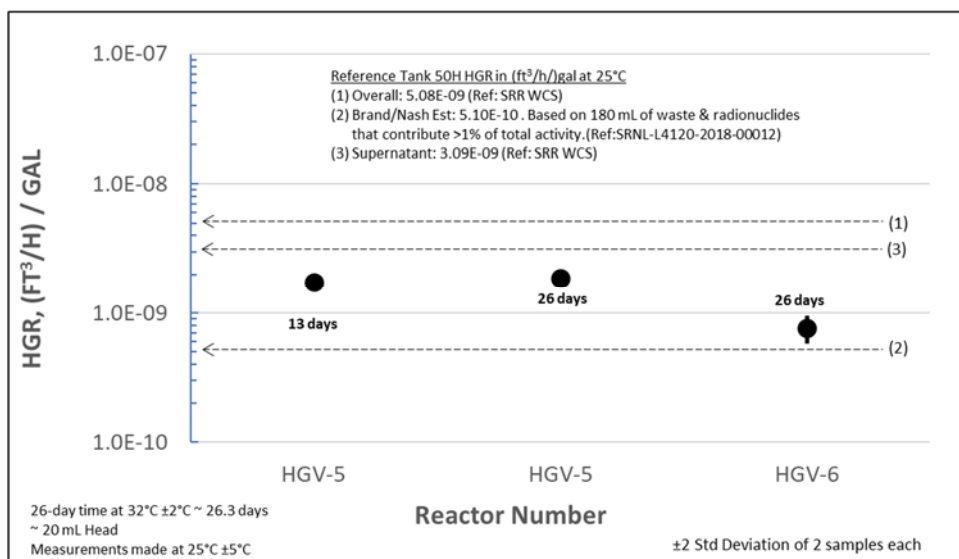**Figure 95. H$_2$ measurements from radioactive-waste Test 6**

Figure 96. HGR measurements from radioactive-waste Test 6

Test 7: Tank 50 waste test at 75°C and other conditions listed in Table 34

Table 34. Seventh Tank 50 Radioactive Test

Spike Type	Reactor Used	Fill Gas	Temperature °C	Amount of liquid, mL	Duration days
BFS	HGV-2	Air, No H_2	75	100	>6
Grout-premix	HGV-3	Air, No H_2	75	100	>6
None, Control	HGV-4	Air, No H_2	75	100	>6
BFS	HGV-5	Air, No H_2	75	100	>6
Grout-premix	HGV-6	Air, No H_2	75	100	>6

The last radioactive test was performed at the 75°C and over 6 days. This temperature represents the projected maximum curing temperature for the new style of SDUs as well as a near centroid, e.g., 32°C to 113°C, in the experimental design. It basically repeated Test 4 but over a longer period with duplicates of BFS and grout-premix. Because the 26-day test was completed by the start of test 7 then all five radioactive sealed reactors were available for use.

Figure 97 shows that the reactors were heated to an average of 72°C and held for almost 6 days. The dip in the temperature after 4 days was a stopping point to sample a subset of the reactors, reseal and continue for remainder of the test period. Originally, the no spike reactor (HGV-4), one BFS spike reactor (HGV-5), and one Grout spike reactor (HGV-6) were to be sampled after 4 days; however, on sampling HGV-5 a loose fitting caused the pressure to drop to around 7 psig. After the fitting was fixed further sampling of HGV-5 would have totally depleted the head space and thereby loosing that reactor to sample after 6 days. Therefore, the other BFS reactor (HGV-2 was sampled.). This is there reason 4 of the 5 reactors lost pressure on the 4th day. Figure 98 shows the how the pressures increased from about 20 to 30 psig, basically due to water vapor. The data in Figure 99 first segregated into the 4-day measurements and the 6-day measurements and then within each period the order is non-spiked waste, BFS spike, and grout-premix Spike. Adding the spike increased H_2 production. It appears that the grout-premix has a higher production rate than the BFS but given the measurement uncertainty the difference may not be significant. Figure 100 shows the HGR to be on the order of 10^{-8} (ft^3/h)/gal.
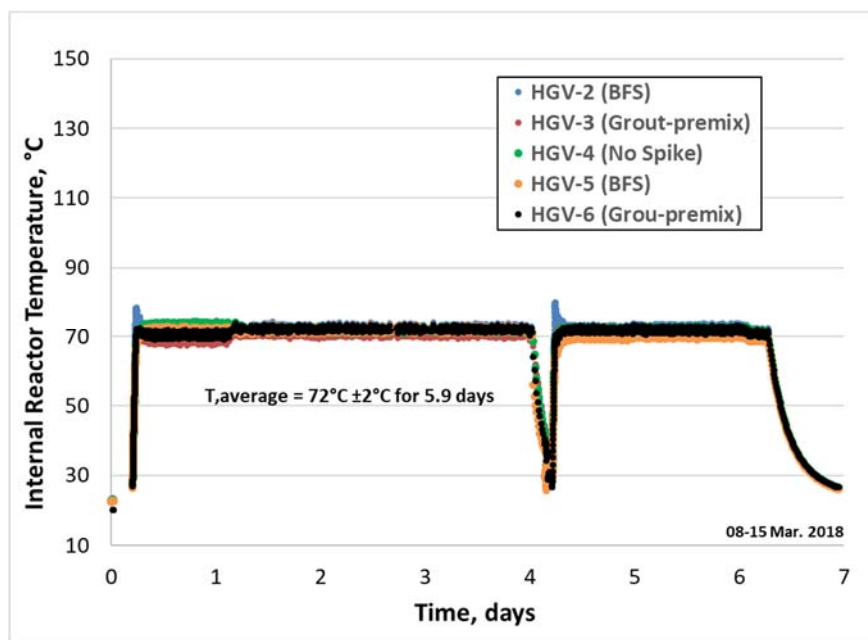

Figure 97. Temperature history of radioactive-waste Test 7
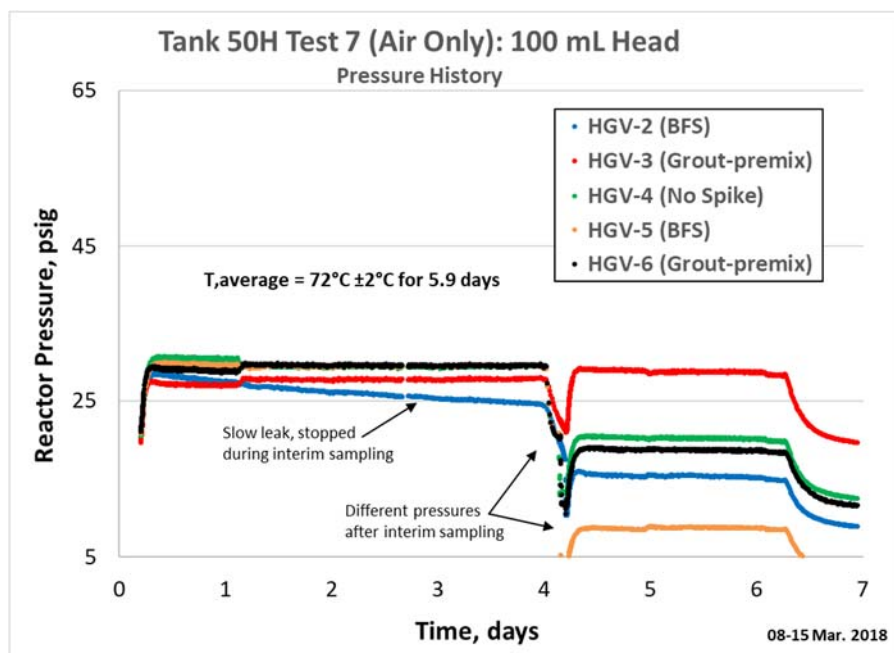
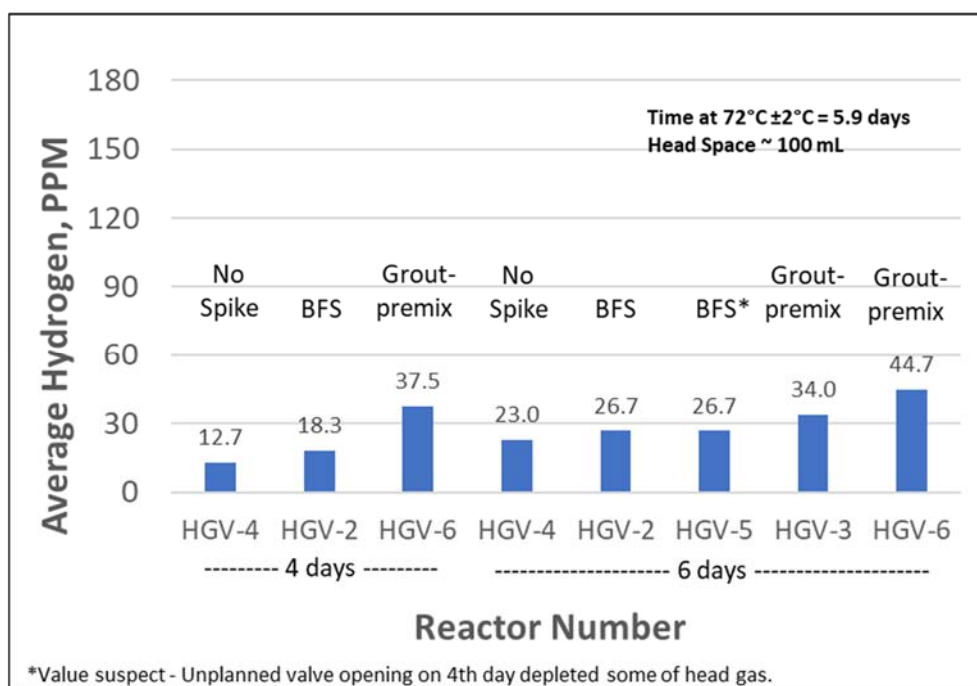**Figure 98. Pressure history of radioactive-waste Test 7**

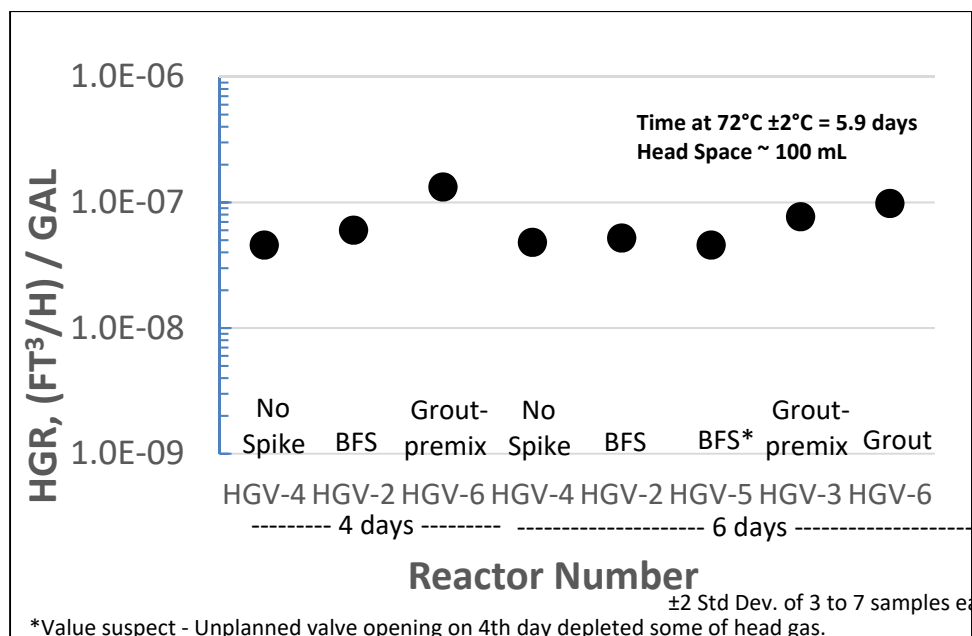**Figure 99. H₂ measurements from radioactive-waste Test 7**

Figure 100. HGR measurements from radioactive-waste Test 7

As noted on the Figure 100, the HGR from HGV-5 for the hydrogen measured on the 6th day is suspect because some of the reactor's head gas was lost on the 4th day and the hydrogen concentration was not measured. In estimating the HGR from the hydrogen measurement on the 6th day it was assumed that the rate was constant from the 4th to the 6th day. This may not be a bad assumption due to results shown from the other reactor, i.e., HGV-2, which contained a BFS spike, too. That is, HGR from HGV-2, measured to have approximately the same rate for 4 and 6-day periods, i.,e., 6.0 x 10^{-8} (ft^3/h)/gal. and 5.2 x 10^{-8} (ft^3/h)/gal., respectively. The HGR from HGV-5 was estimated to be 4.6 x 10^{-8} (ft^3/h)/gal., which is assumed to be a fair value.

Appendix I. WCS Data for Tank 50

This listing of Tank 50 data were entered into WCS (http://prod/WCSOnline/Tanks/TankDetails/50#) on 01/10/2018 for a sample of waste pulled on 07/17/2017. The 07/17/2017is the best available data for the tank to compare to the tank sample pulled on 10/17/2017 that was used for sealed reactor.

50H Tank Details

(Last Updated On : 04-30-2018 11:13)

Whole	Filter details

Flammability

HLLCP Level, HLLCP [*A/C* DSA 3.4.2.11.1 & SAC 5.8.2.44]:
   3.37E+02 in 👤

Safety Analysis Value, SAV [*A/C* SAC 5.8.2.27.a]:
   3.8E-02

⌄Supernate Flammability Temperature, T:
   43 °C

Initial Hydrogen Concentration at 25°C, $y_{o(25C)}$:
   1.52E-03 vol. frac.

Temperature Corrected Initial Hydrogen Concentration, y_o:
   1.49E-03 vol. frac.

Temperature Corrected Hydrogen LFL, LFL_T [*A/C* DSA 3.4.1.1.2]:
   3.92E-02 vol. frac.

Temperature and Organic Corrected Hydrogen LFL, LFL_{OC} [*A/C* DSA 3.4.1.1.2]:
   1.72E-02 vol. frac.

Effective Ion Concentration with Missing Waste, NO_{eff}:
   2.12E+00 M

R_α, R_α:
   3.15E+01 ft^3/MBTU

Alpha Radiolytic Hydrogen Generation Rate:
   2.58E-03 ft^3/hr

$R_{\beta/\gamma}$, $R_{\beta/\gamma}$:
   5.03E+00 ft^3/MBTU

Beta/Gamma Radiolytic Hydrogen Generation Rate:
   4.96E-04 ft^3/hr

Total Radiolytic Hydrogen Generation Rate, x_{RAD}:
   3.08E-03 ft^3/hr

Temperature Corrected Hydrogen Generation Rate, Q_{H2} [*A/C* DSA 3.4.1.1.2]:
   3.26E-03 ft^3/hr

Assumed Tank Level, Flammability Level [*A/C* SAC 5.8.2.44]:
   3.39E+02 in

Vapor Space Volume, V_v [*A/C* SAC 5.8.2.27.a]:
   1.69E+05 gal

Atmospheric Breathing Rate, Q_{ATM} [*A/C* DSA 3.4.1.5.5]:
   4.64E+00 ft^3/hr

Hydrogen Equilibrium Concentration, H_{eq}:
   7.02E-04 vol. frac.

TtLFL, Time to LFL [*A/C* SAC 5.8.2.27.a]:
   NEVER

Radiolytic Time to LFL *[*A/C* SAC 5.8.2.27.a]*:
   NEVER
Spontaneous Time to LFL:
   NEVER
Tank Level Salt Pressure Correction:
   0.0E+00
⌄**LFL Tank Status** *[*A/C* SAC 5.8.2.27.a]*:
   Very Slow
Portable Hydrogen Analyzer Uncertainty *[*A/C* SAC 5.8.2.27.b]*:
   7.65E-02 vol. frac.
Portable Hydrogen Analyzer TSR Concentration Limit, *[*A/C* SAC 5.8.2.27.b]*:
   -8.0E-02 vol. frac.
Total Volumetric Radiolytic Hydrogen Generation Rate *[*A/C* SAC 5.8.2.31 & DSA 3.4.1.1.2]*:
   5.71E-09 ft^3/hr-gal
Supernate Volumetric Radiolytic Hydrogen Generation Rate:
   3.11E-09 ft^3/hr-gal
Spontaneous Hydrogen Release:
   1.22E-03 vol. frac.
Spontaneous Initial Hydrogen Concentration:
   1.49E-03 vol. frac.
⌄**Spontaneous Level Limit**

Appendix J: Uncertainty Analyses

This appendix contains the results from several investigations of the data from the radioactive testing. The measurement equations supporting the HGR calculations are provided and these equations were utilized to estimate the uncertainties of these determinations. An Arrhenius analysis of the HGR values was conducted over the full range of temperatures for the radioactive testing (35 to 114 °C), where these results represent both thermolytic and radiolytic effects on HGR. In addition, an Arrhenius analysis with a focus on the thermolytic effect by adjusting the HGR values for the radiolytic effect was performed. Finally, the effect of the reactor atmosphere (i.e., oxic versus anoxic) on the hydrogen production is investigated.

Hydrogen Generation Rate

The software package GUM Workbench Version 2.4.1.411 [J.1] was utilized to evaluate HGR uncertainties. Initially, the HGR values for test results involving single sampling or the mid-period sampling are considered[*]. The equations utilized to evaluate the uncertainties of these HGR values in this software were:

Equation:

$$A = ((P_{initial} + 14.7)/14.7)*(298.15/(T + 273.15));$$

$$HGR = (H_2 * GC * A * ((RH/1000)*(0.13368/3.785))/1000000)*(1/((RL/1000)*(1/3.785)))*(1/t);$$

where

Quantity	Unit	Definition
A		Correction to 1 atm at 25 oC
$P_{initial}$	psig	initial reactor pressure at sampling
T	oC	temp at sampling
HGR	ft³/(hr-gal)	hydrogen generation rate
H_2	ppm	hydrogen
GC		term to represent the calibration uncertainty for the GC
RH	mL	Reactor Head Space adjusted for stirrer
RL	mL	Reactor Liquid Volume
t	hr	time

and the constants indicated provided the necessary conversion of units. The percent relative standard deviation (%RSD) for the RH and RL volumes was estimated at 1% using the variation seen in the calibration data for the reactor volumes provided in Table 12 of Appendix A. The standard deviations for $P_{initial}$ and T were taken as the maximum of the "Pre Test Uncertainty" values (representing 2 sigma uncertainties) for the thermocouple and pressure instruments, respectively, provided in Table 15 of Appendix B. Using the largest temperature uncertainty from Table 15 is expected to bound the uncertainties in the sampling temperatures across all the reactors.

The GC term in the measurement equation represents the uncertainty of the GC calibrations performed in support of this study. The data used to develop the calibrations and the associated uncertainties are provided in Exhibit J.1. Two calibrations were utilized. An uncertainty for each was determined as a relative standard deviation based upon the square root of the sum of the squares of the relative standard deviations for the H_2

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[*] While only one sampling event was conducted for Test 7 HGV-5, all of the necessary information to evaluate the uncertainty of the HGR resulting from this test in the manner discussed in this appendix was not available. As discussed in the body of the report, the HGR for this test was developed relying upon assumptions whose contribution to the uncertainty of the resulting HGR was not quantifiable.

standard and the measured area. Both resulting uncertainties are about 3% (at 1 sigma). The smaller of the two degrees of freedom values, 27, from the exhibit is utilized in this analysis.

This formula was then utilized to calculate HGR uncertainties for the reactor vessels for the tests using the software package JMP^{TM} Pro Version 11.2.1 [J.2]. An example of the Gum Workbench output for HGV-4 for Test 1 is provided in Exhibit J.2. The HGR values and their uncertainties along with supporting information for each of the reactors for each of the tests as determined using JMP are provided in Table 39 at the end of this appendix. A comparison of the JMP results to those from Gum Workbench for Test 1 HGV-4 demonstrates the accuracy of the JMP output.

Next, the uncertainties of the total HGR values resulting from those tests with a second sampling event were investigated using GUM Workbench Version 2.4.1.411. Specifically, these tests are Test 6 HGV-5 and Test 7 HGV-2, -4, and -6, and the measurement equations and inputs utilized to evaluate the uncertainties of the HGR values resulting from this testing in the software are provided in Exhibits J.3, J.4, J.5, and J.6, respectively. At the end of this appendix, Table 40 provides a summary of the HGR results and their uncertainties.

Arrhenius Analysis of HGR over Full Temperature Range

Once the HGR values were calculated, JMP software was used to explore a model based upon the Arrhenius equation (Equation 2 in the body of the report). For this effort, only data from the oxic testing were used (i.e., the Test 1 results were excluded; a comparison of oxic and anoxic results is provided in a following section). For this approach, the natural logarithms of the HGR values were modeled as a function of the inverse test temperature (1/Kelvin) with the results for each spike/control material (specifically, no spike or control, BFS, and grout-premix) being fitted separately. Both thermolytic and radiolytic effects have an impact on these HGR results; an attempt to focus on the impact of the thermolytic effect is provided in the next section. The resulting fitted models are provided in Exhibit J.7; the exhibit also includes 95% confidence intervals for individual predictions for each of the models.

Based upon the Arrhenius equation the slope of each of these fitted models is a function of the activation energy (E_a) and gas constant (R): slope = E_a/R. Using this relationship and the value for R expressed as 8.314 J/mol/K, the activation energy for each spike material may be determine in the unit kJ/mol as shown in Table 35 below, which also introduces the 95% confidence intervals for the slopes of the fitted models and as a result, 95% confidence intervals for E_a.

**Table 35. Arrhenius Analysis from Radioactive Oxic Testing,
Thermolytic and Radiolytic Effects**

Spike	slope = $-E_a/R$	95% Confidence Interval	
Control	-10298.53	-11865.11	-8731.95
BFS	-8758.89	-11956.11	-5561.67
Grout-premix	-10068.78	-12060.97	-8076.58
	E_a (kJ/mol)	95% Confidence Interval	
Control	85.6	72.6	98.6
BFS	72.8	46.2	99.4
Grout-premix	83.7	67.1	100.3

As seen in Table 35, the confidence intervals for the E_a values for these two spike materials and the control have a great deal of overlap; suggesting that for these tests there does not appear to be any discernible difference in their activation energies. However, even though the slopes are very similar, by looking at the individual grouping of spike data another result may be gleaned. Figure 101 shows a plot of the natural log HGR values grouped by 1/Kelvin values with other descriptive information. The symbol ▲ represents grout-premix, ● represents BFS, and ▼ represents the control (i.e., no spike). It is important to note that

the control points consistently fall just at or below the other data at each of the temperature values except the test at 71.5 °C.
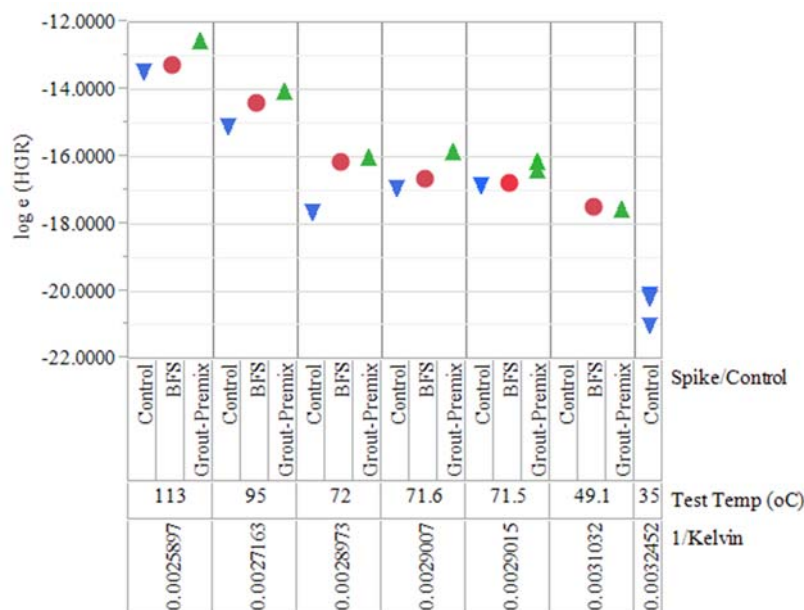

Figure 101. Natural Logarithm HGR Values Grouped by Temperature

Another way to assess these data is to assume (as suggested above) that the activation energy (i.e., the slope) of the Arrhenius expression is the same over these data. Figure 102 provides a fitted model (gray line) derived using all of the data along with the linear fit for the data from each spike separately.
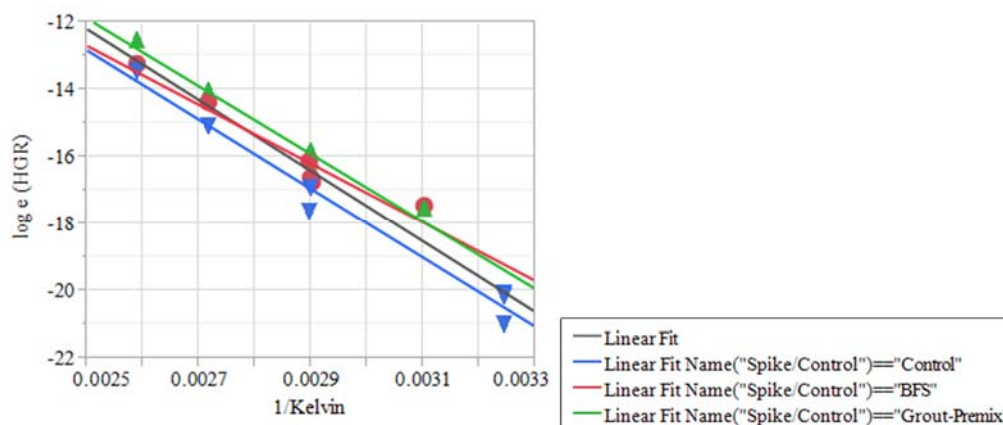

Figure 102. Fitted Models for Arrhenius Equation

There appears to be some difference in these results. Specifically, while the control results may have a similar slope to the results for the grout-premix and BFS spiked testing, there is a somewhat consistent behavior seen in the results for the control versus the results for the others. In general, the control testing leads to lower HGR values for any given temperature.

Exhibit J.8 provides the results from fitting a model that allows for a common slope (i.e., a common activation energy) but looks for a statistical effect due to the spike. The slope from this fitted model is -9935.473 with a 95% confidence interval (-10895.47, -8975.48) leading to an activation energy of 82.6 kJ/mol with a 95% confidence interval (74.6, 90.6). Comparisons of the results across the different spike

materials provided in the exhibit reveal that the control results are statistical lower than those from the grout-premix testing and the grout-premix and BFS results are not statistically different from each other.

Arrhenius Analysis Focused on Thermolytic Effects

The analysis provided in this section is a repeat of that provided in the previous section but with a focus on the thermolytic effects on HGR for these radioactive tests. The approach was to determine the average of the radiolytic HGR results from the 35 °C testing and then to subtract this value from the HGR results for the test temperatures above 35 °C. The result is an estimate of the hydrogen generation from only thermolysis. The adjusted HGR values, that is, the non-radiolytic HGR values, are provided in the 6th column of Table 36 below and were fitted using the Arrhenius model.

Table 36. Test Results for Arrhenius Analysis of Thermolytic Effects

Test	Test Temp (ºC)	Spike/ Control	Reactor	1/Kelvin	HGR - adj- ft3/(hr-gal)	log e (Adj HGR)
Test 2(Air)>06-07Feb	113	Control	HGV-2	0.0025897	1.4188464e-6	-13.4657
Test 2(Air)>06-07Feb	113	BFS	HGV-3	0.0025897	1.7335216e-6	-13.2654
Test 2(Air)>06-07Feb	113	Grout-Premix	HGV-4	0.0025897	3.5543494e-6	-12.5473
Test 3(Air)>12-13Feb	95	Control	HGV-2	0.0027163	2.843463e-7	-15.0731
Test 3(Air)>12-13Feb	95	BFS	HGV-3	0.0027163	5.6104582e-7	-14.3935
Test 3(Air)>12-13Feb	95	Grout-Premix	HGV-4	0.0027163	7.9947123e-7	-14.0393
Test 4(Air)>21-22Feb	72	Control	HGV-2	0.0028973	2.0650022e-8	-17.6955
Test 4(Air)>21-22Feb	72	BFS	HGV-3	0.0028973	9.6923513e-8	-16.1493
Test 4(Air)>21-22Feb	72	Grout-Premix	HGV-4	0.0028973	1.1237958e-7	-16.0014
Test 5(Air)>26-27Feb	49.1	Control	HGV-2	0.0031032	-1.454207e-9	.
Test 5(Air)>26-27Feb	49.1	BFS	HGV-3	0.0031032	2.4611351e-8	-17.5201
Test 5(Air)>26-27Feb	49.1	Grout-Premix	HGV-4	0.0031032	2.2138235e-8	-17.6260
Test 7(Air)>08-15Mar	71.6	BFS	HGV-2	0.0029007	5.867847e-8	-16.6512
Test 7(Air)>08-15Mar	71.6	Control	HGV-4	0.0029007	4.4325756e-8	-16.9317
Test 7(Air)>08-15Mar	71.6	Grout-Premix	HGV-6	0.0029007	1.3130142e-7	-15.8458
Test 7(Air)>08-15Mar	71.5	Grout-Premix	HGV-3	0.0029015	7.5452696e-8	-16.3998
Test 7(Air)>08-15Mar	71.5	BFS	HGV-2	0.0029015	5.1115793e-8	-16.7892
Test 7(Air)>08-15Mar	71.5	Control	HGV-4	0.0029015	4.7175793e-8	-16.8694
Test 7(Air)>08-15Mar	71.5	Grout-Premix	HGV-6	0.0029015	9.7605793e-8	-16.1423

The results of fitting the Arrhenius equation to the data for each spike condition are provided in Exhibit J.9; the exhibit also includes 95% confidence intervals for individual predictions for each of the models. Using the 95% confidence intervals for the slopes of these fitted models leads to the information for the activation energy, E_a, for these tests provided in Table 37 below.

Table 37. Arrhenius Analysis from Radioactive Oxic Testing, Thermolytic Effect Only

	slope = -E_a/R	95% Confidence Interval	
Control	-11801.72	-16267.64	-7335.79
BFS	-8868.15	-12046.05	-5690.25
Grout-premix	-10179.28	-12116.13	-8242.43
	E_a (kJ/mol)	95% Confidence Interval	
Control	98.1	61.0	135.2
BFS	73.7	47.3	100.2
Grout-premix	84.6	68.5	100.7
Exhibit J.10	83.1	71.8	94.3

As seen in Table 37, the confidence intervals for the E_a values for these two spike materials and the control have a great deal of overlap; suggesting that for thermolysis, there does not appear to be any discernible difference in their activation energies. Also, note that the estimated E_a values for the BFS and Grout-premix in Table 37 are similar to their values in Table 35, while there is a larger difference between the E_a values in these tables for the control testing. Exhibit J.10 provides the results from fitting a model that allows for a common slope (i.e., a common activation energy) but looks for a statistical effect due to the spike. The estimated slope from this fitted model is -9992.047 leading to an estimate of the activation energy of 83.1 kJ/mol. (95% confidence intervals are provided in Exhibit J.10 for the slope and in the last row of Table 37 for the activation energy.) Comparisons of the results across the different spike materials provided in the exhibit reveal that the control results are statistically lower than those from the grout-premix testing and the grout-premix and BFS results are not statistically different from each other, nor are the control and BFS results seen to be different.

Effect of Reactor Oxic and Anoxic Atmosphere on Hydrogen

The results from a pair of tests (i.e., Test 1 and Test 2) provide the data that may be used to investigate the impact of changing the vapor space gas chemistry. an effect of reactor atmosphere. The initial approach was to utilize the H_2 ppm values recorded for each of these tests for each of the spike materials. Exhibit J.11 provides the results from this investigation which used JMP to make a statistical comparison of the H_2 values between Test 1 (anoxic – N_2) and Test 2 (oxic – air) for the control, grout-premix, and BFS tests. The results indicate that the average of the H_2 measurements for the oxic test was statistically larger than the average of the H_2 measurements for the anoxic test for the control and the grout-premix spiked reactors. However, the opposite was true for the BFS spiked results: in this comparison, the average of the H_2 measurements for the anoxic test was statistically larger than the average of the H_2 measurements for the oxic test. Figure 103 provides a graphical display of the H_2 values that supports the same conclusions taken from the results provided in Exhibit J.9.
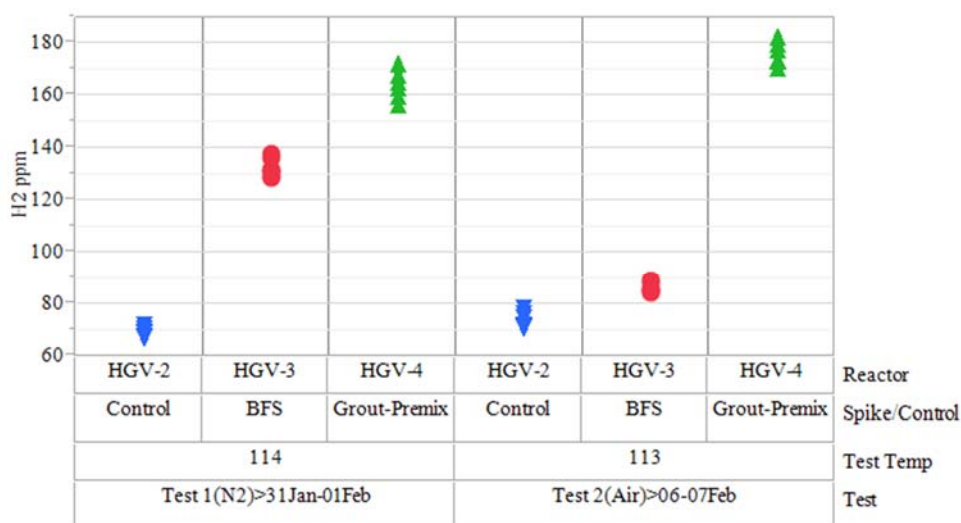

Figure 103. H₂ Values Grouped by Test Vapor Space

Similar comparisons may be made using the HGR values resulting from these tests. Table 38 highlights the HGR values for these tests along with their uncertainties as provided in Table 39.

Table 38. HGR Values and Uncertainty Intervals for Tests 1 (Anoxic) and 2 (Oxic)

Test	Reactor	Spike/ Control	HGR ft^3/(hr-gal)	lower limit (95% confidence)	upper limit (95% confidence)
Test 1(N2)>31Jan-01Feb	HGV-2	Control	1.362E-06	1.266E-06	1.458E-06
Test 1(N2)>31Jan-01Feb	HGV-3	BFS	2.572E-06	2.390E-06	2.754E-06
Test 1(N2)>31Jan-01Feb	HGV-4	Grout-premix	3.396E-06	3.150E-06	3.643E-06
Test 2(Air)>06-07Feb	HGV-2	Control	1.420E-06	1.316E-06	1.525E-06
Test 2(Air)>06-07Feb	HGV-3	BFS	1.735E-06	1.614E-06	1.856E-06
Test 2(Air)>06-07Feb	HGV-4	Grout-premix	3.556E-06	3.306E-06	3.806E-06

While there is overlap in the HGR uncertainty intervals for the anoxic and oxic conditions for both the control and grout-premix testing, for the BFS testing, the uncertainty interval of the HGR result for the anoxic test falls above that for the oxic test.

References

J.1. Metrodata GmbH, "GUM Workbench: User Manual for Version 1.2, 2.3, and 2.4", 2009.

J.2. SAS Institute Inc., JMP™ Pro 11.2.1, Cary, NC, 2014

Exhibit J.1. Estimating the GC Calibration Uncertainty

GC Calibration Used for Test 1

Time	H2 Area	H2 Std conc
2/1/2018 12:59	4463	10.6
2/1/2018 13:03	4591	10.6
2/1/2018 13:06	4689	10.6

H2 conc	10.6	ppm	%RSD	2.5
Ave area	4581			
%Rel Sample Std Dev	2.47			
%RSD (Ave area)	1.73			
RF	0.002313905	conc/area		
% RSD for RF	2.88			
Degrees of freedom	27.8			

GC Calibration Used for Remaining Rad Testing

Time	H2 Area	H2 Std conc
2/6/2018 8:35	5151	10.6
2/6/2018 8:38	5183	10.6
2/6/2018 8:42	5171	10.6
2/6/2018 8:45	4927	10.6
2/6/2018 8:48	4852	10.6
2/6/2018 8:52	4878	10.6
2/6/2018 8:55	5078	10.6

H2 conc	10.6	ppm	%RSD	2.5
Ave area	5034.285714			
%Rel Sample Std Dev	2.87			
%RSD (Ave area)	1.08			
RF	0.002105562	conc/area		
% RSD for RF	2.73			
Degrees of freedom	88.7			

Exhibit J.2. Gum Workbench HGR Uncertainty Results for Test 1 Reactor Vessel HGR-4

Author: b6678

Model Equation:

$$A=((P_{Initial}+14.7)/14.7)*(298.15/(T+273.15));$$

$$HGR=(H_2*GC*A*((RH/1000)*(0.13368/3.785))/1000000)*(1/((RL/1000)*(1/3.785)))*(1/t);$$

List of Quantities:

Quantity	Unit	Definition
A		Correction to 1 atm at 25 oC
$P_{Initial}$	psig	initial reactor pressure at sampling
T	oC	temp at sampling
HGR	ft^3/(hr-gal)	hydrogen generation rate
H_2	ppm	hydrogen
GC		term to represent the calibration uncertainty for the GC
RH	mL	Reactor Head Space adjusted for stirrer
RL	mL	Reactor Liquid Volume
t	hr	time

$P_{Initial}$:   Type B normal distribution
Value: 21.16 psig
Expanded Uncertainty: 0.316 psig
Coverage Factor: 2

T: Type B normal distribution
Value: 20 oC
Expanded Uncertainty: 1.99 oC
Coverage Factor: 2

H_2:   Type A
Method of observation: Direct
Number of observations: 7

No.	Observation
1	172.37 ppm
2	167.75 ppm
3	164.84 ppm
4	163.12 ppm
5	159.7 ppm
6	159.47 ppm
7	156.4 ppm

Arithmetic Mean: 163.38 ppm
Standard Deviation: 5.5 ppm
Standard Uncertainty: 2.07 ppm

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Exhibit J.2. Gum Workbench HGR Uncertainty Results for Test 1 Reactor Vessel HGR-4 *(continued)*

GC: Type B t-distribution
Value: 1
Standard Uncertainty: 3 %
Degrees of Freedom: 27

RH: Type B t-distribution
Value: 99.913 mL
Standard Uncertainty: 1 %
Degrees of Freedom: 6

RL: Type B t-distribution
Value: 93.219 mL
Standard Uncertainty: 1 %
Degrees of Freedom: 6

t: Type B rectangular distribution
Value: 17.1 hr
Halfwidth of Limits: 0.05 hr

Uncertainty Budgets:

A: Correction to 1 atm at 25 oC

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$P_{Initial}$	21.160 psig	0.158 psig	100	normal	0.069	0.011	62.8 %
T	20.000 oC	0.995 oC	100	normal	-0.0085	-0.0084	37.2 %
A	2.4811	0.0138	190				

Date: 06/05/2018	File: HGR Test 1 HGV-4 w GC rev 0.smu	Page 2 of 3

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Exhibit J.2. Gum Workbench HGR Uncertainty Results for Test 1 Reactor Vessel HGR-4 *(continued)*

HGR: hydrogen generation rate

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$P_{Initial}$	21.160 psig	0.158 psig	100	normal	$95 \cdot 10^{-9}$	$15 \cdot 10^{-9}$ $ft^3/(hr\text{-}gal)$	1.5 %
T	20.000 oC	0.995 oC	100	normal	$-12 \cdot 10^{-9}$	$-12 \cdot 10^{-9}$ $ft^3/(hr\text{-}gal)$	0.9 %
H_2	163.38 ppm	2.07 ppm	6	normal	$21 \cdot 10^{-9}$	$43 \cdot 10^{-9}$ $ft^3/(hr\text{-}gal)$	12.4 %
GC	1.0000	0.0300	27	t-distr.	0.0000034	$0.10 \cdot 10^{-6}$ $ft^3/(hr\text{-}gal)$	69.5 %
RH	99.913 mL	0.999 mL	6	t-distr.	$34 \cdot 10^{-9}$	$34 \cdot 10^{-9}$ $ft^3/(hr\text{-}gal)$	7.7 %
RL	93.219 mL	0.932 mL	6	t-distr.	$-36 \cdot 10^{-9}$	$-34 \cdot 10^{-9}$ $ft^3/(hr\text{-}gal)$	7.7 %
t	17.1000 hr	0.0289 hr	infinity	rectangular	$-0.20 \cdot 10^{-6}$	$-5.7 \cdot 10^{-9}$ $ft^3/(hr\text{-}gal)$	0.2 %
HGR	0.000003396 $ft^3/(hr\text{-}gal)$	0.000000122 $ft^3/(hr\text{-}gal)$	44				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
A	2.481	0.028	2.00	95% (t-table 95.45%)
HGR	0.00000340 $ft^3/(hr\text{-}gal)$	7.4 % (relative)	2.06	95% (t-table 95.45%)

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Exhibit J.3. Gum Workbench HGR Results for Second Sample from Test 6 Reactor Vessel HGR-5

Author: b6678

Model Equation:

$P_{Initiala} = P_{Initial} + 14.7;$

$P1a = P1 + 14.7;$

$K1 = T + 273.15;$

$K2 = T2 + 273.15;$

$H2_{moles} = (H_2*GC/1000000)*RH*P_{Initiala}/(1206*K1)*(1-(P1a/P_{Initiala}))+(H_{2b}*GCb/1000000)*P1a*RH/(1206*K2);$

$HGR2 = (H2_{moles}*1206*298.15/14.7)/((2.54*12)^3*t*(RL/3785));$

List of Quantities:

Quantity	Unit	Definition
$P_{Initiala}$	psia	initial reactor pressure at initial sampling
$P_{Initial}$	psig	initial reactor pressure at initial sampling
P1a	psia	initial reactor pressure at final sampling
P1	psig	initial reactor pressure at final sampling
K1	K	temp at initial sampling
T	oC	temp at initial sampling
K2	K	temp at final sampling
T2	oC	temp at final sampling
$H2_{moles}$	g-moles	total g-moles of hydrogen generated by test end
H_2	ppm	hydrogen from initial sample
GC		term to represent the calibration uncertainty for the GC at initial sample measurement
RH	mL	Reactor Head Space adjusted for stirrer
H_{2b}	ppm	hydrogen from final sample
GCb		term to represent the calibration uncertainty for the GC at final sample measurement
HGR2		second HGR
t	hr	time
RL	mL	Reactor Liquid Volume

$P_{Initial}$:   Type B normal distribution
          Value: 20.5 psig
          Expanded Uncertainty: 0.316 psig
          Coverage Factor: 2

P1:   Type B normal distribution
          Value: 6.8 psig
          Expanded Uncertainty: 0.316 psig
          Coverage Factor: 2

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Exhibit J.3. Gum Workbench HGR Results for Second Sample from Test 6 Reactor Vessel HGR-5
(continued)

T:	Type B normal distribution Value: 28 oC Expanded Uncertainty: 1.99 oC Coverage Factor: 2	
T2:	Type B normal distribution Value: 27 oC Expanded Uncertainty: 1.99 oC Coverage Factor: 2	
H_2:	Type A Method of observation: Direct Number of observations: 2	

No.	Observation
1	17.37 ppm
2	16.55 ppm

Arithmetic Mean: 16.960 ppm
Standard Deviation: 0.58 ppm
Standard Uncertainty: 0.410 ppm

GC:	Type B t-distribution Value: 1 Standard Uncertainty: 3 % Degrees of Freedom: 27	
RH:	Type B t-distribution Value: 18.57 mL Standard Uncertainty: 1 % Degrees of Freedom: 6	
H_{2b}:	Type A Method of observation: Direct Number of observations: 2	

No.	Observation
1	47.29 ppm
2	45.44 ppm

Arithmetic Mean: 46.365 ppm
Standard Deviation: 1.3 ppm
Standard Uncertainty: 0.925 ppm

GCb:	Type B t-distribution Value: 1 Standard Uncertainty: 3 % Degrees of Freedom: 27	
t:	Type B rectangular distribution Value: 631.8 hr Halfwidth of Limits: 0.05 hr	

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Exhibit J.3. Gum Workbench HGR Results for Second Sample from Test 6 Reactor Vessel HGR-5
(continued)

RL: Type B t-distribution
        Value: 174.49 mL
        Standard Uncertainty: 1 %
        Degrees of Freedom: 6

Interim Results:

Quantity	Value	Standard Uncertainty	Degrees of Freedom
$P_{Initiala}$	35.200 psia	0.158 psia	100
P1a	21.500 psia	0.158 psia	100
K1	301.150 K	0.995 K	100
K2	300.150 K	0.995 K	100
$H2_{moles}$	$63.02 \cdot 10^{-9}$ g-moles	$2.03 \cdot 10^{-9}$ g-moles	12

Uncertainty Budgets:

HGR2:   second HGR

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$P_{Initiala}$	35.200 psia	0.158 psia	100				
$P_{Initial}$	20.500 psig	0.158 psig	100	normal	$26 \cdot 10^{-12}$	$4.1 \cdot 10^{-12}$	0.4 %
P1a	21.500 psia	0.158 psia	100				
P1	6.800 psig	0.158 psig	100	normal	$45 \cdot 10^{-12}$	$7.1 \cdot 10^{-12}$	1.3 %
K1	301.150 K	0.995 K	100				
T	28.000 oC	0.995 oC	100	normal	$-1.2 \cdot 10^{-12}$	$-1.2 \cdot 10^{-12}$	0.0 %
K2	300.150 K	0.995 K	100				
T2	27.000 oC	0.995 oC	100	normal	$-5.1 \cdot 10^{-12}$	$-5.0 \cdot 10^{-12}$	0.6 %
$H2_{moles}$	$63.02 \cdot 10^{-9}$ g-moles	$2.03 \cdot 10^{-9}$ g-moles	12				
H_2	16.960 ppm	0.410 ppm	1	normal	$21 \cdot 10^{-12}$	$8.5 \cdot 10^{-12}$	1.8 %
GC	1.0000	0.0300	27	t-distr.	$350 \cdot 10^{-12}$	$11 \cdot 10^{-12}$	2.8 %
RH	18.570 mL	0.186 mL	6	t-distr.	$100 \cdot 10^{-12}$	$19 \cdot 10^{-12}$	8.8 %
H_{2b}	46.365 ppm	0.925 ppm	1	normal	$33 \cdot 10^{-12}$	$30 \cdot 10^{-12}$	23.1 %
GCb	1.0000	0.0300	27	t-distr.	$1.5 \cdot 10^{-9}$	$46 \cdot 10^{-12}$	52.3 %
t	631.8000 hr	0.0289 hr	infinity	rectangular	$-3.0 \cdot 10^{-12}$	$-85 \cdot 10^{-15}$	0.0 %
RL	174.49 mL	1.74 mL	6	t-distr.	$-11 \cdot 10^{-12}$	$-19 \cdot 10^{-12}$	8.8 %
HGR2	$1.8690 \cdot 10^{-9}$	$0.0629 \cdot 10^{-9}$	15				

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Exhibit J.3. Gum Workbench HGR Results for Second Sample from Test 6 Reactor Vessel HGR-5
(continued)

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
HGR2	$1.87 \cdot 10^{-9}$	7.3 % (relative)	2.18	95% (t-table 95.45%)

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Exhibit J.4. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-2

Author: b6678

Model Equation:

$P_{Initiala} = P_{Initial} + 14.7;$

$P1a = P1 + 14.7;$

$K1 = T + 273.15;$

$K2 = T2 + 273.15;$

$H2_{moles} = (H_2 * GC/1000000) * RH * P_{Initiala}/(1206*K1)*(1-(P1a/P_{Initiala})) + (H_{2b}*GCb/1000000)*P1a*RH/(1206*K2);$

$HGR2 = (H2_{moles}*1206*298.15/14.7)/((2.54*12)^3*t*(RL/3785));$

List of Quantities:

Quantity	Unit	Definition
$P_{Initiala}$	psia	initial reactor pressure at initial sampling
$P_{Initial}$	psig	initial reactor pressure at initial sampling
P1a	psia	initial reactor pressure at final sampling
P1	psig	initial reactor pressure at final sampling
K1	K	temp at initial sampling
T	oC	temp at initial sampling
K2	K	temp at final sampling
T2	oC	temp at final sampling
$H2_{moles}$	g-moles	total g-moles of hydrogen generated by test end
H_2	ppm	hydrogen from initial sample
GC		term to represent the calibration uncertainty for the GC at initial sample measurement
RH	mL	Reactor Head Space adjusted for stirrer
H_{2b}	ppm	hydrogen from final sample
GCb		term to represent the calibration uncertainty for the GC at final sample measurement
HGR2		second HGR
t	hr	time
RL	mL	Reactor Liquid Volume

$P_{Initial}$: Type B normal distribution
Value: 17.2 psig
Expanded Uncertainty: 0.316 psig
Coverage Factor: 2

P1: Type B normal distribution
Value: 8.7 psig
Expanded Uncertainty: 0.316 psig
Coverage Factor: 2

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Exhibit J.4. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-2
(continued)

T:
Type B normal distribution
Value: 30 oC
Expanded Uncertainty: 1.99 oC
Coverage Factor: 2

T2:
Type B normal distribution
Value: 27 oC
Expanded Uncertainty: 1.99 oC
Coverage Factor: 2

H_2:
Type A
Method of observation: Direct
Number of observations: 3

No.	Observation
1	18.08 ppm
2	18.63 ppm
3	18.04 ppm

Arithmetic Mean: 18.250 ppm
Standard Deviation: 0.33 ppm
Standard Uncertainty: 0.190 ppm

GC:
Type B t-distribution
Value: 1
Standard Uncertainty: 3 %
Degrees of Freedom: 27

RH:
Type B t-distribution
Value: 99.29 mL
Standard Uncertainty: 1 %
Degrees of Freedom: 6

H_{2b}:
Type A
Method of observation: Direct
Number of observations: 7

No.	Observation
1	26.39 ppm
2	27.24 ppm
3	27.01 ppm
4	25.66 ppm
5	26.68 ppm
6	26.68 ppm
7	27.43 ppm

Arithmetic Mean: 26.727 ppm
Standard Deviation: 0.59 ppm
Standard Uncertainty: 0.223 ppm

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Exhibit J.4. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-2
(continued)

GCb: Type B t-distribution
Value: 1
Standard Uncertainty: 3 %
Degrees of Freedom: 27

t: Type B rectangular distribution
Value: 140.63 hr
Halfwidth of Limits: 0.05 hr

RL: Type B t-distribution
Value: 94.5 mL
Standard Uncertainty: 1 %
Degrees of Freedom: 6

Interim Results:

Quantity	Value	Standard Uncertainty	Degrees of Freedom
$P_{Initiala}$	31.900 psia	0.158 psia	100
P1a	23.400 psia	0.158 psia	100
K1	303.150 K	0.995 K	100
K2	300.150 K	0.995 K	100
$H2_{moles}$	$213.68 \cdot 10^{-9}$ g-moles	$6.00 \cdot 10^{-9}$ g-moles	42

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Exhibit J.4. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-2
(continued)

Uncertainty Budgets:

HGR2:   second HGR

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$P_{Initiala}$	31.900 psia	0.158 psia	100				
$P_{Initial}$	17.200 psig	0.158 psig	100	normal	$1.2 \cdot 10^{-9}$	$190 \cdot 10^{-12}$	1.5 %
P1a	23.400 psia	0.158 psia	100				
P1	8.700 psig	0.158 psig	100	normal	$580 \cdot 10^{-12}$	$92 \cdot 10^{-12}$	0.3 %
K1	303.150 K	0.995 K	100				
T	30.000 oC	0.995 oC	100	normal	$-34 \cdot 10^{-12}$	$-34 \cdot 10^{-12}$	0.0 %
K2	300.150 K	0.995 K	100				
T2	27.000 oC	0.995 oC	100	normal	$-140 \cdot 10^{-12}$	$-140 \cdot 10^{-12}$	0.8 %
$H2_{moles}$	$213.68 \cdot 10^{-9}$ g-moles	$6.00 \cdot 10^{-9}$ g-moles	42				
H_2	18.250 ppm	0.190 ppm	2	normal	$570 \cdot 10^{-12}$	$110 \cdot 10^{-12}$	0.5 %
GC	1.0000	0.0300	27	t-distr.	$10 \cdot 10^{-9}$	$310 \cdot 10^{-12}$	3.9 %
RH	99.290 mL	0.993 mL	6	t-distr.	$530 \cdot 10^{-12}$	$530 \cdot 10^{-12}$	11.3 %
H_{2b}	26.727 ppm	0.223 ppm	6	normal	$1.6 \cdot 10^{-9}$	$350 \cdot 10^{-12}$	5.1 %
GCb	1.0000	0.0300	27	t-distr.	$42 \cdot 10^{-9}$	$1.3 \cdot 10^{-9}$	65.3 %
t	140.6300 hr	0.0289 hr	infinity	rectangular	$-370 \cdot 10^{-12}$	$-11 \cdot 10^{-12}$	0.0 %
RL	94.500 mL	0.945 mL	6	t-distr.	$-560 \cdot 10^{-12}$	$-530 \cdot 10^{-12}$	11.3 %
HGR2	$52.57 \cdot 10^{-9}$	$1.57 \cdot 10^{-9}$	48				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
HGR2	$52.6 \cdot 10^{-9}$	6.1 % (relative)	2.06	95% (t-table 95.45%)

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Exhibit J.5. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-4

Author: b6678

Model Equation:

$P_{Initiala} = P_{Initial} + 14.7;$

$P1a = P1 + 14.7;$

$K1 = T + 273.15;$

$K2 = T2 + 273.15;$

$H2_{moles} = (H_2 * GC/1000000) * RH * P_{Initiala}/(1206*K1)*(1-(P1a/P_{Initiala})) + (H_{2b}*GCb/1000000)*P1a*RH/(1206*K2);$

$HGR2 = (H2_{moles}*1206*298.15/14.7)/((2.54*12)^3*t*(RL/3785));$

List of Quantities:

Quantity	Unit	Definition
$P_{Initiala}$	psia	initial reactor pressure at initial sampling
$P_{Initial}$	psig	initial reactor pressure at initial sampling
P1a	psia	initial reactor pressure at final sampling
P1	psig	initial reactor pressure at final sampling
K1	K	temp at initial sampling
T	oC	temp at initial sampling
K2	K	temp at final sampling
T2	oC	temp at final sampling
$H2_{moles}$	g-moles	total g-moles of hydrogen generated by test end
H_2	ppm	hydrogen from initial sample
GC		term to represent the calibration uncertainty for the GC at initial sample measurement
RH	mL	Reactor Head Space adjusted for stirrer
H_{2b}	ppm	hydrogen from final sample
GCb		term to represent the calibration uncertainty for the GC at final sample measurement
HGR2		second HGR
t	hr	time
RL	mL	Reactor Liquid Volume

$P_{Initial}$: Type B normal distribution
Value: 20.5 psig
Expanded Uncertainty: 0.316 psig
Coverage Factor: 2

P1: Type B normal distribution
Value: 12.2 psig
Expanded Uncertainty: 0.316 psig
Coverage Factor: 2

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Exhibit J.5. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-4
(continued)

T: Type B normal distribution
Value: 30 oC
Expanded Uncertainty: 1.99 oC
Coverage Factor: 2

T2: Type B normal distribution
Value: 25 oC
Expanded Uncertainty: 1.99 oC
Coverage Factor: 2

H_2: Type A
Method of observation: Direct
Number of observations: 3

No.	Observation
1	12.62 ppm
2	13.21 ppm
3	12.35 ppm

Arithmetic Mean: 12.727 ppm
Standard Deviation: 0.44 ppm
Standard Uncertainty: 0.254 ppm

GC: Type B t-distribution
Value: 1
Standard Uncertainty: 3 %
Degrees of Freedom: 27

RH: Type B t-distribution
Value: 98.48 mL
Standard Uncertainty: 1 %
Degrees of Freedom: 6

H_{2b}: Type A
Method of observation: Direct
Number of observations: 7

No.	Observation
1	23.24 ppm
2	23.46 ppm
3	23.43 ppm
4	23.67 ppm
5	22.30 ppm
6	23.30 ppm
7	21.68 ppm

Arithmetic Mean: 23.011 ppm
Standard Deviation: 0.73 ppm
Standard Uncertainty: 0.277 ppm

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Exhibit J.5. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-4
(continued)

GCb: Type B t-distribution
Value: 1
Standard Uncertainty: 3 %
Degrees of Freedom: 27

t: Type B rectangular distribution
Value: 140.63 hr
Halfwidth of Limits: 0.05 hr

RL: Type B t-distribution
Value: 94.66 mL
Standard Uncertainty: 1 %
Degrees of Freedom: 6

Interim Results:

Quantity	Value	Standard Uncertainty	Degrees of Freedom
$P_{Initiala}$	35.200 psia	0.158 psia	100
P1a	26.900 psia	0.158 psia	100
K1	303.150 K	0.995 K	100
K2	298.150 K	0.995 K	100
$H2_{moles}$	$0.19799 \cdot 10^{-6}$ g-moles	$0.00599 \cdot 10^{-6}$ g-moles	42

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Exhibit J.5. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-4
(continued)

Uncertainty Budgets:

HGR2: second HGR

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$P_{initiala}$	35.200 psia	0.158 psia	100				
$P_{initial}$	20.500 psig	0.158 psig	100	normal	$0.84 \cdot 10^{-9}$	$0.13 \cdot 10^{-9}$	0.7 %
P1a	26.900 psia	0.158 psia	100				
P1	12.200 psig	0.158 psig	100	normal	$0.71 \cdot 10^{-9}$	$0.11 \cdot 10^{-9}$	0.5 %
K1	303.150 K	0.995 K	100				
T	30.000 oC	0.995 oC	100	normal	$-23 \cdot 10^{-12}$	$-23 \cdot 10^{-12}$	0.0 %
K2	298.150 K	0.995 K	100				
T2	25.000 oC	0.995 oC	100	normal	$-0.14 \cdot 10^{-9}$	$-0.14 \cdot 10^{-9}$	0.8 %
$H2_{moles}$	$0.19799 \cdot 10^{-6}$ g-moles	$0.00599 \cdot 10^{-6}$ g-moles	42				
H_2	12.727 ppm	0.254 ppm	2	normal	$0.55 \cdot 10^{-9}$	$0.14 \cdot 10^{-9}$	0.8 %
GC	1.0000	0.0300	27	t-distr.	$7.0 \cdot 10^{-9}$	$0.21 \cdot 10^{-9}$	1.8 %
RH	98.480 mL	0.985 mL	6	t-distr.	$0.49 \cdot 10^{-9}$	$0.49 \cdot 10^{-9}$	9.9 %
H_{2b}	23.011 ppm	0.277 ppm	6	normal	$1.8 \cdot 10^{-9}$	$0.50 \cdot 10^{-9}$	10.5 %
GCb	1.0000	0.0300	27	t-distr.	$42 \cdot 10^{-9}$	$1.2 \cdot 10^{-9}$	65.1 %
t	140.6300 hr	0.0289 hr	infinity	rectangular	$-0.35 \cdot 10^{-9}$	$-10 \cdot 10^{-12}$	0.0 %
RL	94.660 mL	0.947 mL	6	t-distr.	$-0.51 \cdot 10^{-9}$	$-0.49 \cdot 10^{-9}$	9.9 %
HGR2	$48.63 \cdot 10^{-9}$	$1.55 \cdot 10^{-9}$	48				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
HGR2	$48.6 \cdot 10^{-9}$	6.6 % (relative)	2.06	95% (t-table 95.45%)

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Exhibit J.6. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-6

Author: b6678

Model Equation:

$P_{Initiala} = P_{Initial} + 14.7;$

$P1a = P1 + 14.7;$

$K1 = T + 273.15;$

$K2 = T2 + 273.15;$

$H2_{moles} = (H_2*GC/1000000)*RH*P_{Initiala}/(1206*K1)*(1-(P1a/P_{Initiala})) + (H_{2b}*GCb/1000000)*P1a*RH/(1206*K2);$

$HGR2 = (H2_{moles}*1206*298.15/14.7)/((2.54*12)^3*t*(RL/3785));$

List of Quantities:

Quantity	Unit	Definition
$P_{Initiala}$	psia	initial reactor pressure at initial sampling
$P_{Initial}$	psig	initial reactor pressure at initial sampling
P1a	psia	initial reactor pressure at final sampling
P1	psig	initial reactor pressure at final sampling
K1	K	temp at initial sampling
T	oC	temp at initial sampling
K2	K	temp at final sampling
T2	oC	temp at final sampling
$H2_{moles}$	g-moles	total g-moles of hydrogen generated by test end
H_2	ppm	hydrogen from initial sample
GC		term to represent the calibration uncertainty for the GC at initial sample measurement
RH	mL	Reactor Head Space adjusted for stirrer
H_{2b}	ppm	hydrogen from final sample
GCb		term to represent the calibration uncertainty for the GC at final sample measurement
HGR2		second HGR
t	hr	time
RL	mL	Reactor Liquid Volume

$P_{Initial}$: Type B normal distribution
Value: 20.1 psig
Expanded Uncertainty: 0.316 psig
Coverage Factor: 2

P1: Type B normal distribution
Value: 11.1 psig
Expanded Uncertainty: 0.316 psig
Coverage Factor: 2

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Exhibit J.6. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-6
(continued)

T: Type B normal distribution
Value: 28 oC
Expanded Uncertainty: 1.99 oC
Coverage Factor: 2

T2: Type B normal distribution
Value: 24 oC
Expanded Uncertainty: 1.99 oC
Coverage Factor: 2

H_2: Type A
Method of observation: Direct
Number of observations: 3

No.	Observation
1	38.05 ppm
2	37.4 ppm
3	37.14 ppm

Arithmetic Mean: 37.530 ppm
Standard Deviation: 0.47 ppm
Standard Uncertainty: 0.271 ppm

GC: Type B t-distribution
Value: 1
Standard Uncertainty: 3 %
Degrees of Freedom: 27

RH: Type B t-distribution
Value: 98.64 mL
Standard Uncertainty: 1 %
Degrees of Freedom: 6

H_{2b}: Type A
Method of observation: Direct
Number of observations: 7

No.	Observation
1	47.33 ppm
2	45.9 ppm
3	45.45 ppm
4	44.81 ppm
5	43.88 ppm
6	42.28 ppm
7	42.91 ppm

Arithmetic Mean: 44.651 ppm
Standard Deviation: 1.8 ppm
Standard Uncertainty: 0.666 ppm

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Exhibit J.6. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-6
(continued)

GCb: Type B t-distribution
Value: 1
Standard Uncertainty: 3 %
Degrees of Freedom: 27

t: Type B rectangular distribution
Value: 140.63 hr
Halfwidth of Limits: 0.05 hr

RL: Type B t-distribution
Value: 95.95 mL
Standard Uncertainty: 1 %
Degrees of Freedom: 6

Interim Results:

Quantity	Value	Standard Uncertainty	Degrees of Freedom
$P_{Initiala}$	34.800 psia	0.158 psia	100
$P1a$	25.800 psia	0.158 psia	100
K1	301.150 K	0.995 K	100
K2	297.150 K	0.995 K	100
$H2_{moles}$	$0.4088 \cdot 10^{-5}$ g-moles	$0.0119 \cdot 10^{-5}$ g-moles	45

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Exhibit J.6. Gum Workbench HGR Results for Second Sample from Test 7 Reactor Vessel HGR-6
(continued)

Uncertainty Budgets:

HGR2:   second HGR

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$P_{Initiala}$	34.800 psia	0.158 psia	100				
$P_{Initial}$	20.100 psig	0.158 psig	100	normal	$2.5 \cdot 10^{-9}$	$0.39 \cdot 10^{-9}$	1.6 %
P1a	25.800 psia	0.158 psia	100				
P1	11.100 psig	0.158 psig	100	normal	$0.51 \cdot 10^{-9}$	$80 \cdot 10^{-12}$	0.0 %
K1	301.150 K	0.995 K	100				
T	28.000 oC	0.995 oC	100	normal	$-74 \cdot 10^{-12}$	$-73 \cdot 10^{-12}$	0.0 %
K2	297.150 K	0.995 K	100				
T2	24.000 oC	0.995 oC	100	normal	$-0.26 \cdot 10^{-9}$	$-0.26 \cdot 10^{-9}$	0.7 %
$H2_{moles}$	$0.4088 \cdot 10^{-6}$ g-moles	$0.0119 \cdot 10^{-6}$ g-moles	45				
H_2	37.530 ppm	0.271 ppm	2	normal	$0.59 \cdot 10^{-9}$	$0.16 \cdot 10^{-9}$	0.3 %
GC	1.0000	0.0300	27	t-distr.	$22 \cdot 10^{-9}$	$0.67 \cdot 10^{-9}$	4.8 %
RH	98.640 mL	0.986 mL	6	t-distr.	$1.0 \cdot 10^{-9}$	$0.99 \cdot 10^{-9}$	10.6 %
H_{2b}	44.651 ppm	0.666 ppm	6	normal	$1.7 \cdot 10^{-9}$	$1.1 \cdot 10^{-9}$	14.1 %
GCb	1.0000	0.0300	27	t-distr.	$77 \cdot 10^{-9}$	$2.3 \cdot 10^{-9}$	57.2 %
t	140.6300 hr	0.0289 hr	infinity	rectangular	$-0.70 \cdot 10^{-9}$	$-20 \cdot 10^{-12}$	0.0 %
RL	95.950 mL	0.960 mL	6	t-distr.	$-1.0 \cdot 10^{-9}$	$-0.99 \cdot 10^{-9}$	10.6 %
HGR2	$99.06 \cdot 10^{-9}$	$3.05 \cdot 10^{-9}$	51				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
HGR2	$99.1 \cdot 10^{-9}$	6.3 % (relative)	2.05	95% (t-table 95.45%)

Generated with GUM Workbench Pro Version 2.4.1.411

Exhibit J.7. Fitting of the Arrhenius Equation for the Test Results over the Full Temperature Range for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix)

Bivariate Fit of log e (HGR) By 1/Kelvin Spike/Control=Control
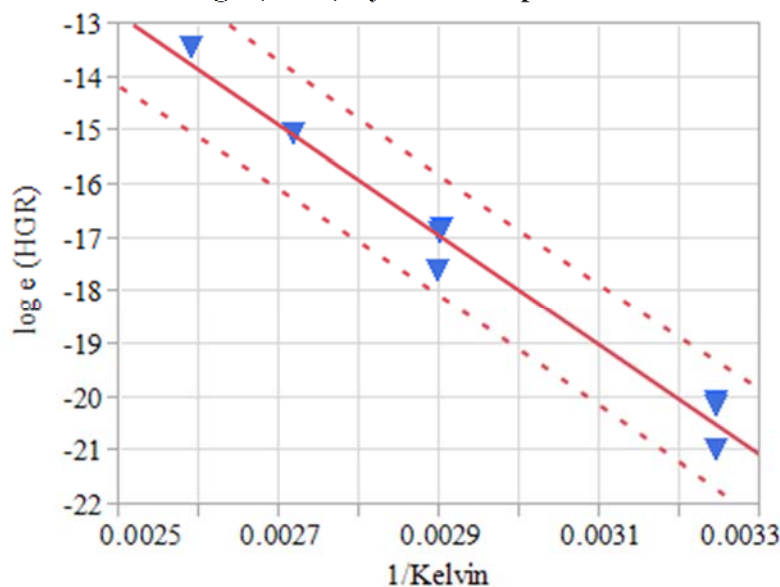
Linear Fit

Linear Fit
log e (HGR) = 12.916721 - 10298.529*1/Kelvin

Summary of Fit

RSquare	0.977337
RSquare Adj	0.97356
Root Mean Square Error	0.42992
Mean of Response	-17.6453
Observations (or Sum Wgts)	8

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	4	0.6215414	0.155385	0.6376
Pure Error	2	0.4874446	0.243722	**Prob > F**
Total Error	6	1.1089860		0.6859
				Max RSq

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	47.825295	47.8253	258.7515
Error	6	1.108986	0.1848	**Prob > F**
C. Total	7	48.934281		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	12.916721	1.906016	6.78	0.0005*	8.252869	17.580574
1/Kelvin	-10298.53	640.2267	-16.09	<.0001*	-11865.11	-8731.95

Dotted Lines form a 95% confidence interval for an individual prediction

Exhibit J.7. Fitting of the Arrhenius Equation for the Test Results over the Full Temperature Range for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix)
(continued)

Bivariate Fit of log e (HGR) By 1/Kelvin Spike/Control=BFS
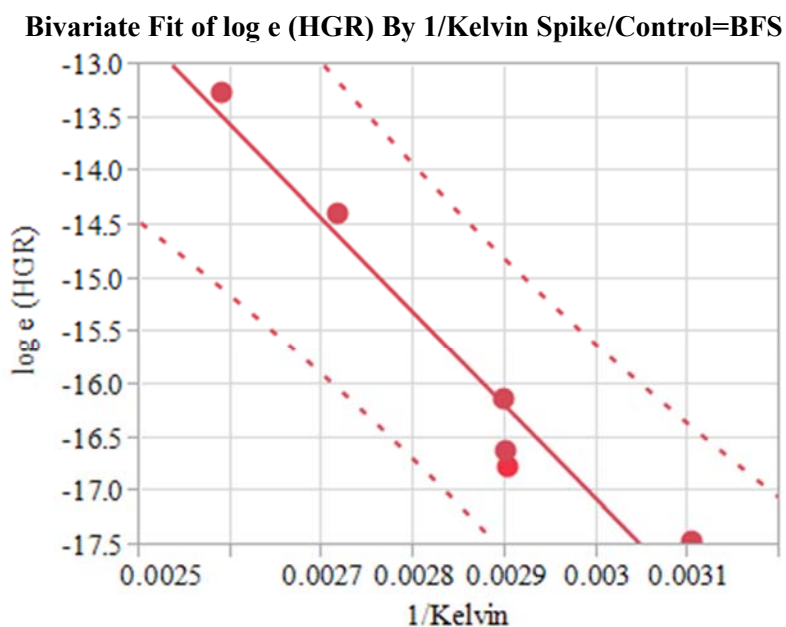
⎯⎯ Linear Fit

Linear Fit

log e (HGR) = 9.2019601 - 8758.8903*1/Kelvin

Summary of Fit

RSquare	0.935331
RSquare Adj	0.919164
Root Mean Square Error	0.456566
Mean of Response	-15.7734
Observations (or Sum Wgts)	6

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	12.059721	12.0597	57.8537
Error	4	0.833809	0.2085	**Prob > F**
C. Total	5	12.893530		0.0016*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	9.2019601	3.288855	2.80	0.0489*	0.0706345	18.333286
1/Kelvin	-8758.89	1151.552	-7.61	0.0016*	-11956.11	-5561.668

Dotted Lines form a 95% confidence interval for an individual prediction

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Exhibit J.7. Fitting of the Arrhenius Equation for the Test Results over the Full Temperature Range for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix)
(continued)

Bivariate Fit of log e (HGR) By 1/Kelvin Spike/Control=Grout-Premix

────── Linear Fit

Linear Fit

log e (HGR) = 13.285511 - 10068.775*1/Kelvin

Summary of Fit

RSquare	0.97123
RSquare Adj	0.965476
Root Mean Square Error	0.309362
Mean of Response	-15.4969
Observations (or Sum Wgts)	7

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	4	0.44648666	0.111622	3.4841
Pure Error	1	0.03203742	0.032037	**Prob > F**
Total Error	5	0.47852408		0.3795
				Max RSq

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	16.154296	16.1543	168.7929
Error	5	0.478524	0.0957	**Prob > F**
C. Total	6	16.632820		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	13.285511	2.218472	5.99	0.0019*	7.5827464	18.988276
1/Kelvin	-10068.78	774.9961	-12.99	<.0001*	-12060.97	-8076.584

Dotted Lines form a 95% confidence interval for an individual prediction

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Exhibit J.8. Fitting of the Arrhenius Equation for the Test Results over the Full Temperature Range with an Additional Model Term for the Type of Spike/Control

Response log e (HGR) Whole Model Regression Plot

Actual by Predicted Plot

Residual by Predicted Plot

Summary of Fit	
RSquare	0.972696
RSquare Adj	0.967878
Root Mean Square Error	0.398615
Mean of Response	-16.3943
Observations (or Sum Wgts)	21

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	96.230604	32.0769	201.8758
Error	17	2.701200	0.1589	**Prob > F**
C. Total	20	98.931804		<.0001*

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	14	2.1817175	0.155837	0.9000
Pure Error	3	0.5194820	0.173161	**Prob > F**
Total Error	17	2.7011995		0.6223
				Max RSq

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	12.433556	1.319056	9.43	<.0001*	9.6505919	15.21652
1/Kelvin	-9935.473	455.0133	-21.84	<.0001*	-10895.47	-8975.479
Spike/Control[Control]	-0.594244	0.124334	-4.78	0.0002*	-0.856566	-0.331923
Spike/Control[BFS]	0.1233446	0.129803	0.95	0.3553	-0.150516	0.3972054

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Spike/Control	2	2	4.148482	13.0542	0.0004*
1/Kelvin	1	1	75.759432	476.7920	<.0001*

Spike/Control
LSMeans Differences Tukey HSD

Level		Least Sq Mean
Grout-Premix	A	-15.88927
BFS	A	-16.23683
Control	B	-16.95442

Levels not connected by same letter are significantly different.

Exhibit J.9. Fitting of the Arrhenius Equation with Adjusted HGR Values for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix)

Bivariate Fit of log e (Adj HGR) By 1/Kelvin Spike/Control=Control
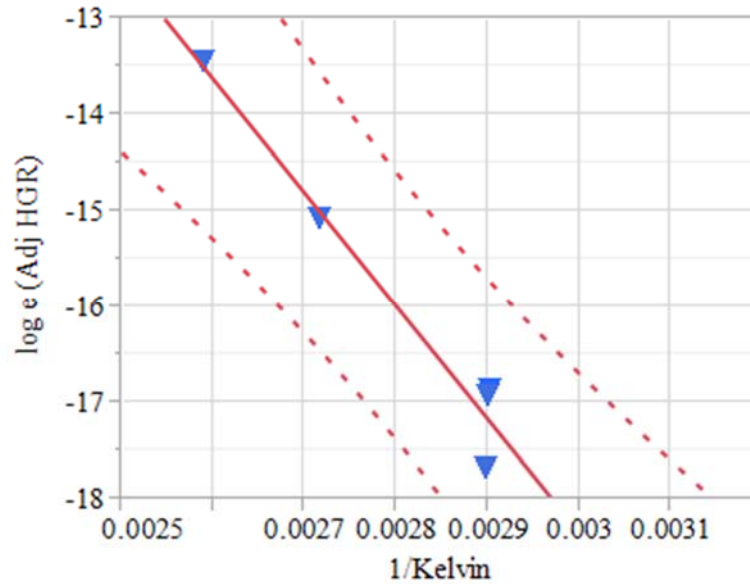
—— Linear Fit

Linear Fit

log e (Adj HGR) = 17.050449 - 11801.715*1/Kelvin

Summary of Fit

RSquare	0.95931
RSquare Adj	0.945746
Root Mean Square Error	0.399731
Mean of Response	-16.0071
Observations (or Sum Wgts)	5

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	11.301219	11.3012	70.7278
Error	3	0.479354	0.1598	**Prob > F**
C. Total	4	11.780573		0.0035*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	17.050449	3.934812	4.33	0.0227*	4.5281204	29.572778
1/Kelvin	-11801.72	1403.299	-8.41	0.0035*	-16267.64	-7335.792

Dotted Lines form a 95% confidence interval for an individual prediction

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Exhibit J.9. Fitting of the Arrhenius Equation with Adjusted HGR Values for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix) *(continued)*

Bivariate Fit of log e (Adj HGR) By 1/Kelvin Spike/Control=BFS

──── Linear Fit

Linear Fit

log e (Adj HGR) = 9.4921378 - 8868.1527*1/Kelvin

Summary of Fit

RSquare	0.937529
RSquare Adj	0.921911
Root Mean Square Error	0.453806
Mean of Response	-15.7948
Observations (or Sum Wgts)	6

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	12.362475	12.3625	60.0295
Error	4	0.823760	0.2059	**Prob > F**
C. Total	5	13.186235		0.0015*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	9.4921378	3.268977	2.90	0.0440*	0.4160018	18.568274
1/Kelvin	-8868.153	1144.592	-7.75	0.0015*	-12046.05	-5690.255

Dotted Lines form a 95% confidence interval for an individual prediction

Exhibit J.9. Fitting of the Arrhenius Equation with Adjusted HGR Values for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix) *(continued)*

Bivariate Fit of log e (Adj HGR) By 1/Kelvin Spike/Control=Grout-Premix
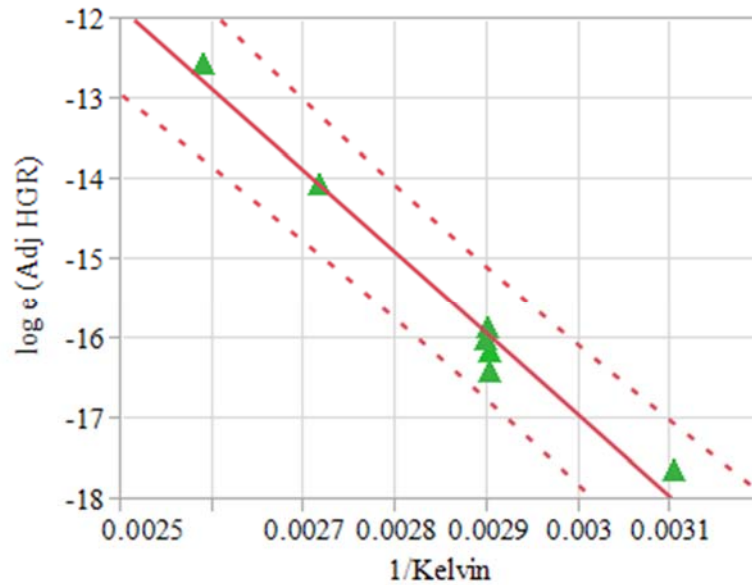
Linear Fit

Linear Fit

log e (Adj HGR) = 13.583735 - 10179.278*1/Kelvin

Summary of Fit

RSquare	0.973336
RSquare Adj	0.968003
Root Mean Square Error	0.300768
Mean of Response	-15.5146
Observations (or Sum Wgts)	7

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	16.510821	16.5108	182.5176
Error	5	0.452308	0.0905	**Prob > F**
C. Total	6	16.963129		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	13.583735	2.156846	6.30	0.0015*	8.0393868	19.128083
1/Kelvin	-10179.28	753.4675	-13.51	<.0001*	-12116.13	-8242.428

Dotted Lines form a 95% confidence interval for an individual prediction

Exhibit J.10. Fitting of the Arrhenius with Adjusted HGR Values with an Additional Model Term for the Type of Spike/Control

Response log e (HGR) Whole Model Regression Plot

Actual by Predicted Plot

log e (Adj HGR) Predicted P<.0001
RSq=0.95 RMSE=0.3987

Residual by Predicted Plot

log e (Adj HGR) Predicted

Summary of Fit

RSquare	0.947837
RSquare Adj	0.936659
Root Mean Square Error	0.398685
Mean of Response	-15.7448
Observations (or Sum Wgts)	18

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	40.434667	13.4782	84.7956
Error	14	2.225292	0.1589	**Prob > F**
C. Total	17	42.659959		<.0001*

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	13	2.1921571	0.168627	5.0891
Pure Error	1	0.0331353	0.033135	**Prob > F**
Total Error	14	2.2252925		0.3352
				Max RSq

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	Lower 95%	Upper 95%
Intercept	12.575595	1.796113	7.00	<.0001*	8.723316	16.427874
1/Kelvin	-9992.047	632.2129	-15.80	<.0001*	-11348.01	-8636.085
Spike/Control[BFS]	0.1212452	0.133836	0.91	0.3803	-0.165805	0.4082952
Spike/Control[Grout-Premix]	0.4729245	0.129435	3.65	0.0026*	0.1953142	0.7505347

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
1/Kelvin	1	1	39.704645	249.7941	<.0001*
Spike/Control	2	2	3.271743	10.2918	0.0018*

Spike/Control
LSMeans Differences Tukey HSD

Level		Least Sq Mean
Grout-Premix	A	-15.33113
BFS	A	-15.68281
Control	B	-16.39822

Levels not connected by same letter are significantly different.

Exhibit J.11. Comparison of Generated H₀ for Oxic (Test 2) and Anoxic (Test 1) for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix)

Oneway Analysis of H2 ppm by Test Spike=Control
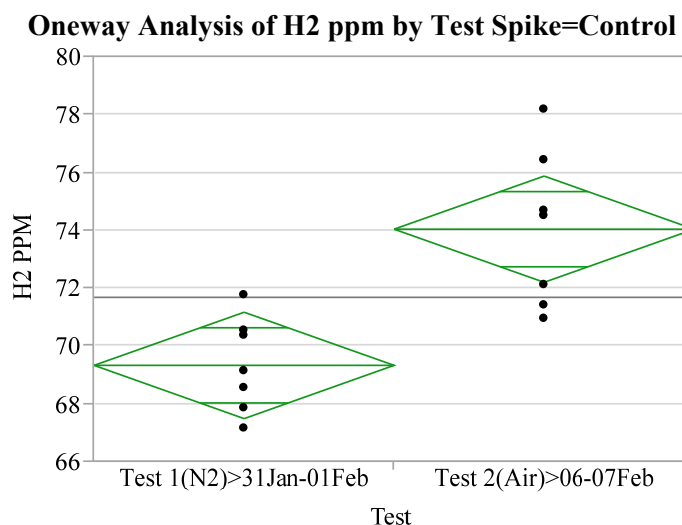
Oneway Anova
Summary of Fit

Rsquare	0.564751
Adj Rsquare	0.528481
Root Mean Square Error	2.232403
Mean of Response	71.69571
Observations (or Sum Wgts)	14

t Test
Test 2(Air)>06-07Feb-Test 1(N2)>31Jan-01Feb
Assuming equal variances

Difference	4.70857	t Ratio	3.945941
Std Err Dif	1.19327	DF	12
Upper CL Dif	7.30848	Prob > |t|	0.0019*
Lower CL Dif	2.10866	Prob > t	0.0010*
Confidence	0.95	Prob < t	0.9990

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Test	1	77.59726	77.5973	15.5704	0.0019*
Error	12	59.80349	4.9836		
C. Total	13	137.40074			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Test 1(N2)>31Jan-01Feb	7	69.3414	0.84377	67.503	71.180
Test 2(Air)>06-07Feb	7	74.0500	0.84377	72.212	75.888

Std Error uses a pooled estimate of error variance

Exhibit J.11. Comparison of Generated H₀ for Oxic (Test 2) and Anoxic (Test 1) for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix) *(continued)*

Oneway Analysis of H2 ppm by Test Spike=Grout-premix
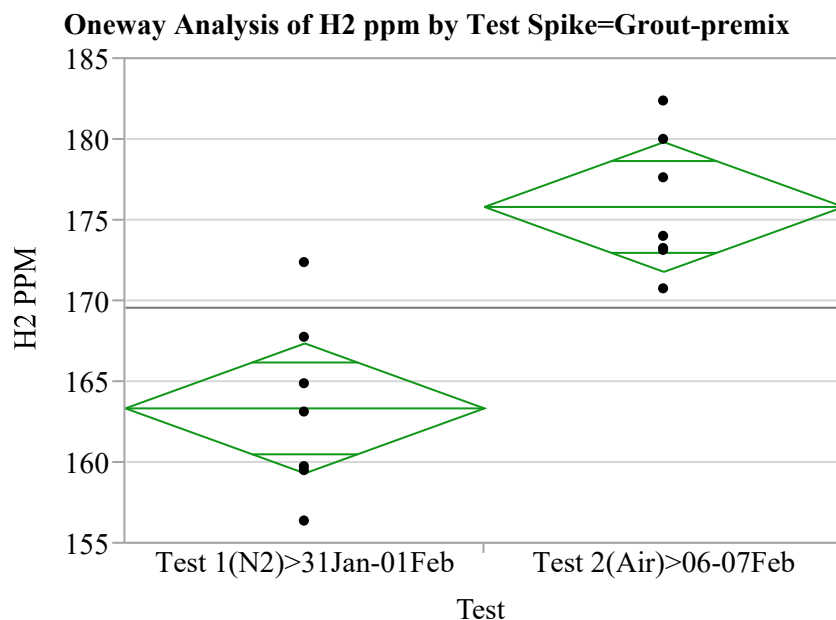
Oneway Anova Summary of Fit

Rsquare	0.655486
Adj Rsquare	0.626777
Root Mean Square Error	4.881261
Mean of Response	169.6121
Observations (or Sum Wgts)	14

t Test

Test 2(Air)>06-07Feb-Test 1(N2)>31Jan-01Feb
Assuming equal variances

Difference	12.4671	t Ratio	4.778251	
Std Err Dif	2.6091	DF	12	
Upper CL Dif	18.1520	Prob > |t|	0.0004*	
Lower CL Dif	6.7823	Prob > t	0.0002*	
Confidence	0.95	Prob < t	0.9998	

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Test	1	544.00378	544.004	22.8317	0.0004*
Error	12	285.92046	23.827		
C. Total	13	829.92424			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Test 1(N2)>31Jan-01Feb	7	163.379	1.8449	159.36	167.40
Test 2(Air)>06-07Feb	7	175.846	1.8449	171.83	179.87

Std Error uses a pooled estimate of error variance

Exhibit J.11. Comparison of Generated H₀ for Oxic (Test 2) and Anoxic (Test 1) for Each Type of Spike/Control (i.e., Control, BFS, and Grout-premix)
(continued)

Oneway Analysis of H2 ppm by Test Spike=BFS
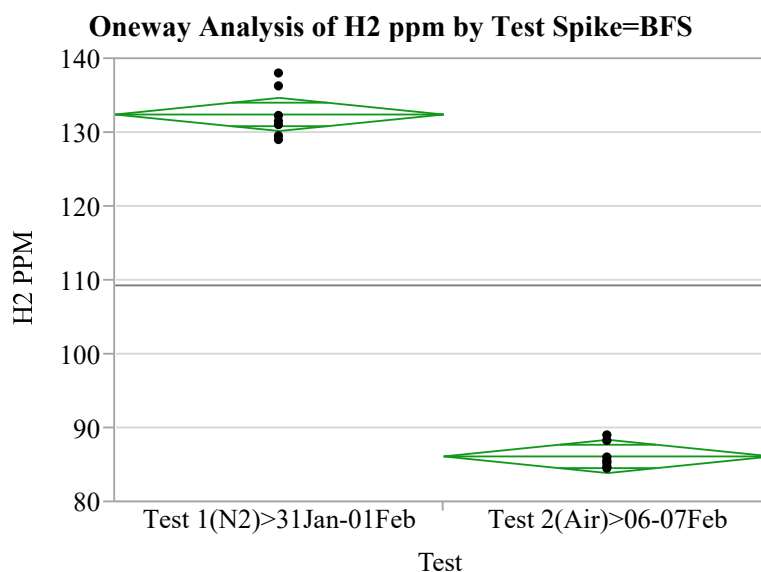
Oneway Anova
Summary of Fit

Rsquare	0.988224
Adj Rsquare	0.987242
Root Mean Square Error	2.729097
Mean of Response	109.3629
Observations (or Sum Wgts)	14

t Test
Test 2(Air)>06-07Feb-Test 1(N2)>31Jan-01Feb
Assuming equal variances

Difference	-46.291	t Ratio	-31.7333	
Std Err Dif	1.459	DF	12	
Upper CL Dif	-43.113	Prob > |t|	<.0001*	
Lower CL Dif	-49.470	Prob > t	1.0000	
Confidence	0.95	Prob < t	<.0001*	

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Test	1	7500.1373	7500.14	1007.004	<.0001*
Error	12	89.3756	7.45		
C. Total	13	7589.5129			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Test 1(N2)>31Jan-01Feb	7	132.509	1.0315	130.26	134.76
Test 2(Air)>06-07Feb	7	86.217	1.0315	83.97	88.46

Std Error uses a pooled estimate of error variance

Table 39. HGR and Uncertainty Determinations for Single and Mid-Period Measurement Testing with Inputs and JMP Details

Test	Test Temp (°C)	Spike/ Control	Reactor	1/Kelvin	HGR ft3/(hr-gal)	Std Dev HGR	Degrees of Freedom (DOF) for HGR std dev	%RSD HGR	Lower Limit (95% confidence)	Upper Limit (95% confidence)	log e (HGR)
Test 1(N2)>31Jan-01Feb	114	Control	HGV-2	0.0025829782	1.3618416e-6	4.7459067e-8	42.9	3.5%	1.2661228e-6	1.4575603e-6	-13.5067
Test 1(N2)>31Jan-01Feb	114	BFS	HGV-3	0.0025829782	2.5723741e-6	9.0274933e-8	43.5	3.5%	2.3903748e-6	2.7543734e-6	-12.8707
Test 1(N2)>31Jan-01Feb	114	Grout-premix	HGV-4	0.0025829782	3.3963882e-6	1.2217801e-7	44.5	3.6%	3.1502348e-6	3.6425416e-6	-12.5928
Test 2(Air)>06-07Feb	113	Control	HGV-2	0.0025896672	0.0000014203	5.1733715e-8	44.8	3.6%	1.3160881e-6	1.5245132e-6	-13.4646
Test 2(Air)>06-07Feb	113	BFS	HGV-3	0.0025896672	1.7349758e-6	5.9935866e-8	42.0	3.5%	1.6140205e-6	1.8559311e-6	-13.2645
Test 2(Air)>06-07Feb	113	Grout-premix	HGV-4	0.0025896672	3.5558037e-6	1.2409545e-7	43.1	3.5%	3.3055505e-6	3.8060568e-6	-12.5469
Test 3(Air)>12-13Feb	95	Control	HGV-2	0.0027162841	2.8580051e-7	1.0109693e-8	44.0	3.5%	2.6542622e-7	3.061748e-7	-15.0680
Test 3(Air)>12-13Feb	95	BFS	HGV-3	0.0027162841	0.0000005625	2.0130669e-8	44.5	3.6%	5.2194171e-7	6.0305835e-7	-14.3909
Test 3(Air)>12-13Feb	95	Grout-premix	HGV-4	0.0027162841	8.0092544e-7	2.766816e-8	42.0	3.5%	7.4508893e-7	8.5676195e-7	-14.0375
Test 4(Air)>21-22Feb	72	Control	HGV-2	0.002897291	2.2104229e-8	1.8469964e-9	8.5	8.4%	1.7888769e-8	2.6319689e-8	-17.6275
Test 4(Air)>21-22Feb	72	BFS	HGV-3	0.002897291	9.837772e-8	4.0099952e-9	34.6	4.1%	9.0233411e-8	1.0652203e-7	-16.1345
Test 4(Air)>21-22Feb	72	Grout-premix	HGV-4	0.002897291	1.1383378e-7	4.5470601e-9	37.0	4.0%	1.0462024e-7	1.2304733e-7	-15.9885
Test 5(Air)>26-27Feb	49.1	Control	HGV-2	0.0031031808	0	0	.	.	.	.	.
Test 5(Air)>26-27Feb	49.1	BFS	HGV-3	0.0031031808	2.6065558e-8	2.5954454e-9	7.6	10.0%	2.0029004e-8	3.2102113e-8	-17.4627
Test 5(Air)>26-27Feb	49.1	Grout-premix	HGV-4	0.0031031808	2.3592443e-8	1.4703007e-9	11.6	6.2%	2.037815e-8	2.6806735e-8	-17.5623
Test 6(Air)>06Feb-05Mar	35	Control	HGV-5	0.0032451728	1.7274398e-9	7.154771e-11	7.9	4.1%	1.5619015e-9	1.8929782e-9	-20.1766
Test 6(Air)>06Feb-05Mar	35	Control	HGV-6	0.0032451728	7.661816e-10	5.338655e-11	5.1	7.0%	6.294311e-10	9.029322e-10	-20.9896
Test 7(Air)>08-15Mar	71.6	BFS	HGV-2	0.0029006526	6.0132678e-8	2.121055e-9	39.4	3.5%	5.5843938e-8	6.4421417e-8	-16.6267
Test 7(Air)>08-15Mar	71.6	Control	HGV-4	0.0029006526	4.5779963e-8	1.7901862e-9	20.8	3.9%	4.2054559e-8	4.9505366e-8	-16.8994
Test 7(Air)>08-15Mar	71.6	Grout-premix	HGV-6	0.0029006526	1.3275562e-7	4.5673501e-9	40.4	3.4%	1.2352741e-7	1.4198383e-7	-15.8348
Test 7(Air)>08-15Mar	71.5	Grout-premix	HGV-3	0.0029014943	7.6906904e-8	2.8788238e-9	43.3	3.7%	7.1102311e-8	8.2711496e-8	-16.3807

Table 39. HGR and Uncertainty Determinations for Single and Mid-Period Measurement Testing with Inputs and JMP Details *(continued)*

Test	Reactor	Initial Pressure at Sampling (psig)	Std Dev Initial Pressure (psig)	Reactor Temp at Sampling (°C)	Std Dev Reactor Temp (°C)	N Rows	Mean (H2 ppm)	Std Dev (H2 ppm)	Reactor Liquid (ml)	Reactor Liquid (gal)
Test 1(N2)>31Jan-01Feb	HGV-2	20.53	0.158	20	0.995	7	69.341428571	1.6406647898	95.43	0.025212682
Test 1(N2)>31Jan-01Feb	HGV-3	19.98	0.158	20	0.995	7	132.50857143	3.4431740617	95.54	0.025241744
Test 1(N2)>31Jan-01Feb	HGV-4	21.16	0.158	20	0.995	7	163.37857143	5.4721581013	93.22	0.024628798
Test 2(Air)>06-07Feb	HGV-2	18.47	0.158	22	0.995	7	74.05	2.6973072993	95.65	0.025270806
Test 2(Air)>06-07Feb	HGV-3	20.23	0.158	22	0.995	7	86.217142857	1.7437002254	96.14	0.025400264
Test 2(Air)>06-07Feb	HGV-4	19.26	0.158	22	0.995	7	175.84571429	4.2081938214	93.91	0.024811096
Test 3(Air)>12-13Feb	HGV-2	18.84	0.158	22	0.995	7	16.617142857	0.4720774755	95.0757	0.025119075
Test 3(Air)>12-13Feb	HGV-3	19.56	0.158	22	0.995	7	32.221428571	1.0291003931	95.6911	0.025281664
Test 3(Air)>12-13Feb	HGV-4	19.56	0.158	22	0.995	7	45.265714286	0.9146375811	94.409	0.024942933
Test 4(Air)>21-22Feb	HGV-2	19.12	0.158	23	0.995	7	1.3885714286	0.2809168662	95.35344	0.025192454
Test 4(Air)>21-22Feb	HGV-3	20.73	0.158	23	0.995	7	5.9428571429	0.361373043	96.02013	0.025368594
Test 4(Air)>21-22Feb	HGV-4	20.25	0.158	23	0.995	7	6.8085714286	0.3871015617	94.24762	0.024900296
Test 5(Air)>26-27Feb	HGV-2	19.13	0.158	23	0.995	7	0	0	95.46653	0.025222333
Test 5(Air)>26-27Feb	HGV-3	21.89	0.158	23	0.995	7	1.5857142857	0.3931860095	95.70477	0.025285276
Test 5(Air)>26-27Feb	HGV-4	21.3	0.158	23	0.995	7	1.4214285714	0.1972670416	93.82029	0.024787395
Test 6(Air)>06Feb-05Mar	HGV-5	20.5	0.158	28	0.995	2	16.96	0.5798275606	174.49	0.046100396
Test 6(Air)>06Feb-05Mar	HGV-6	21.6	0.158	27	0.995	4	13.4825	1.6457900838	175.3829	0.046336301
Test 7(Air)>08-15Mar	HGV-2	17.21	0.158	30	0.995	3	18.25	0.3296968304	94.5048	0.024968243
Test 7(Air)>08-15Mar	HGV-4	20.48	0.158	30	0.995	3	12.726666667	0.4398105653	94.6565	0.025008322
Test 7(Air)>08-15Mar	HGV-6	20.08	0.158	28	0.995	3	37.53	0.4687216658	95.9507	0.025350251
Test 7(Air)>08-15Mar	HGV-3	19.33	0.158	26	0.995	7	33.972857143	1.4729303478	95.6696	0.025275984

Table 39. HGR and Uncertainty Determinations for Single and Mid-Period Measurement Testing with Inputs and JMP Details (*continued*)

Test	Reactor	Nominal Reactor Head ml	Stirrer ml	Reactor Head Adjusted ml	Reactor Head ft3	Duration (hr) at Temp	A (correction to 1 atm at 25 °C)	Std Dev RH	Std Dev RL	Std Dev Time	GC	Std Dev GC	Std Dev DOF for GC
Test 1(N2)>31Jan-01Feb	HGV-2	101.0753528	2.717695	98.3576578	0.003473831	17.1	2.4374753005	0.983576578	0.9543	0.0289	1	0.03	27
Test 1(N2)>31Jan-01Feb	HGV-3	101.5954033	2.717695	98.8777083	0.003492199	17.1	2.3994221806	0.988777083	0.9554	0.0289	1	0.03	27
Test 1(N2)>31Jan-01Feb	HGV-4	102.6309562	2.717695	99.9132612	0.003528773	17.1	2.4810634197	0.999132612	0.9322	0.0289	1	0.03	27
Test 2(Air)>06-07Feb	HGV-2	100.8565978	2.717695	98.1389028	0.003466105	16.3	2.2793980001	0.981389028	0.9565	0.0289	1	0.03	27
Test 2(Air)>06-07Feb	HGV-3	100.9946758	2.717695	98.2769808	0.003470982	16.3	2.4003428442	0.982769808	0.9614	0.0289	1	0.03	27
Test 2(Air)>06-07Feb	HGV-4	101.9371001	2.717695	99.2194051	0.003504267	16.3	2.3336857426	0.992194051	0.9391	0.0289	1	0.03	27
Test 3(Air)>12-13Feb	HGV-2	101.4331	2.717695	98.715405	0.003486466	18.6	2.3048239048	0.98715405	0.950757	0.0289	1	0.03	27
Test 3(Air)>12-13Feb	HGV-3	101.4442	2.717695	98.726505	0.003486858	18.6	2.3543013411	0.98726505	0.956911	0.0289	1	0.03	27
Test 3(Air)>12-13Feb	HGV-4	101.4412	2.717695	98.723505	0.003486752	18.6	2.3543013411	0.98723505	0.94409	0.0289	1	0.03	27
Test 4(Air)>21-22Feb	HGV-2	101.15539	2.717695	98.437695	0.003476658	20.08	2.3162175355	0.98437695	0.9535344	0.0289	1	0.03	27
Test 4(Air)>21-22Feb	HGV-3	101.11521	2.717695	98.397515	0.003475239	20.08	2.4264809959	0.98397515	0.9602013	0.0289	1	0.03	27
Test 4(Air)>21-22Feb	HGV-4	101.60258	2.717695	98.884885	0.003492452	20.08	2.3936074176	0.98884885	0.9424762	0.0289	1	0.03	27
Test 5(Air)>26-27Feb	HGV-2	101.04229	2.717695	98.324595	0.003472664	21.02	2.3169024017	0.98324595	0.9546653	0.0289	1	0.03	27
Test 5(Air)>26-27Feb	HGV-3	101.43057	2.717695	98.712875	0.003486377	21.02	2.5059254767	0.98712875	0.9570477	0.0289	1	0.03	27
Test 5(Air)>26-27Feb	HGV-4	102.02991	2.717695	99.312215	0.003507545	21.02	2.4655183701	0.99312215	0.9382029	0.0289	1	0.03	27
Test 6(Air)>06Feb-05Mar	HGV-5	21.28	2.717695	18.562305	0.00065559	331	2.3707036858	0.18562305	1.7449	0.0289	1	0.03	27
Test 6(Air)>06Feb-05Mar	HGV-6	21.921	2.717695	19.203305	0.000678229	631.8	2.4529333972	0.19203305	1.753829	0.0289	1	0.03	27
Test 7(Air)>08-15Mar	HGV-2	102.0041	2.717695	99.286405	0.003506633	91	2.1349450946	0.99286405	0.945048	0.0289	1	0.03	27
Test 7(Air)>08-15Mar	HGV-5	101.1937	2.717695	98.476005	0.003478011	91	2.3537251153	0.98476005	0.946565	0.0289	1	0.03	27
Test 7(Air)>08-15Mar	HGV-6	101.3532	2.717695	98.635505	0.003483644	91	2.3424168804	0.98635505	0.959507	0.0289	1	0.03	27
Test 7(Air)>08-15Mar	HGV-3	101.4657	2.717695	98.748005	0.003487618	140.63	2.3072275074	0.98748005	0.956696	0.0289	1	0.03	27

Table 39. HGR and Uncertainty Determinations for Single and Mid-Period Measurement Testing with Inputs and JMP Details *(continued)*

Test	Reactor	Partial HGR wrt H2	Partial HGR wrt RH	Partial HGR wrt RL	Partial HGR wrt Time	Partial A wrt P_initial	Partial A wrt T	Partial HGR wrt P_initial	Partial HGR wrt T	Partial HGR wrt GC
Test 1(N2)>31Jan-01Feb	HGV-2	1.9639653e-8	1.3845811e-8	-1.427058e-8	-7.963986e-8	0.0691874908	-0.008314772	3.8655736e-8	-4.645545e-9	1.3618416e-6
Test 1(N2)>31Jan-01Feb	HGV-3	1.9412888e-8	2.6015713e-8	-2.692458e-8	-1.504312e-7	0.0691874908	-0.008184964	7.4174569e-8	-8.774941e-9	2.5723741e-6
Test 1(N2)>31Jan-01Feb	HGV-4	2.0788456e-8	3.3993367e-8	-3.643411e-8	-1.986192e-7	0.0691874908	-0.00846346	9.4712443e-8	-1.158584e-8	3.3963882e-6
Test 2(Air)>06-07Feb	HGV-2	1.9180292e-8	1.4472351e-8	-1.484894e-8	-8.713501e-8	0.0687186614	-0.007722846	4.2818831e-8	-4.812132e-9	0.0000014203
Test 2(Air)>06-07Feb	HGV-3	2.0123328e-8	1.7653939e-8	-1.804635e-8	-1.064402e-7	0.0687186614	-0.00813262	4.9670078e-8	-5.878285e-9	1.7349758e-6
Test 2(Air)>06-07Feb	HGV-4	2.0221156e-8	3.5837784e-8	-3.786395e-8	-2.181475e-7	0.0687186614	-0.007906779	1.0470564e-7	-1.204745e-8	3.5558037e-6
Test 3(Air)>12-13Feb	HGV-2	1.7199136e-8	2.8951966e-9	-3.006031e-9	-1.536562e-8	0.0687186614	-0.007808992	8.5211839e-9	-9.68323e-10	2.8580051e-7
Test 3(Air)>12-13Feb	HGV-3	1.7457327e-8	5.6975584e-9	-5.87829e-9	-3.024194e-8	0.0687186614	-0.007976627	1.6418565e-8	-1.905811e-9	0.0000005625
Test 3(Air)>12-13Feb	HGV-4	1.7693865e-8	8.1128141e-9	-8.483571e-9	-4.306051e-8	0.0687186614	-0.007976627	2.3377859e-8	-2.713622e-9	8.0092544e-7
Test 4(Air)>21-22Feb	HGV-2	1.5918683e-8	2.245505e-10	-2.31814e-10	-1.100808e-9	0.0684866214	-0.007821056	6.535845e-10	-7.46386e-11	2.2104229e-8
Test 4(Air)>21-22Feb	HGV-3	1.6553943e-8	9.997988e-10	-1.024553e-9	-4.899289e-9	0.0684866214	-0.008193419	2.7766785e-9	-3.32189e-10	9.837772e-8
Test 4(Air)>21-22Feb	HGV-4	1.6719188e-8	1.1511748e-9	-1.207816e-9	-5.669013e-9	0.0684866214	-0.008082416	3.2570467e-9	-3.84379e-10	1.1383378e-7
Test 5(Air)>26-27Feb	HGV-2	1.5175831e-8	0	0	0	0.0684866214	-0.007823408	0	0	0
Test 5(Air)>26-27Feb	HGV-3	1.643774e-8	2.640543e-10	-2.72354e-10	-1.240036e-9	0.0684866214	-0.008461676	7.123684e-10	-8.80147e-11	2.6065558e-8
Test 5(Air)>26-27Feb	HGV-4	1.6597698e-8	2.375583e-10	-2.51464e-10	-1.122381e-9	0.0684866214	-0.008325235	6.553456e-10	-7.96638e-11	2.3592443e-8
Test 6(Air)>06Feb-05Mar	HGV-5	1.018538e-10	9.306171e-11	-9.89994e-12	-5.21885e-12	0.0673495365	-0.007872169	4.9075e-11	-5.73614e-12	1.7274398e-9
Test 6(Air)>06Feb-05Mar	HGV-6	5.682786e-11	3.989843e-11	-4.36862e-12	-1.2127e-12	0.0675739228	-0.008172358	2.110693e-11	-2.55266e-12	7.661816e-10
Test 7(Air)>08-15Mar	HGV-2	3.2949412e-9	6.056487e-10	-6.36292e-10	-6.60799e-10	0.0669052051	-0.007042537	1.8844462e-9	-1.98359e-10	6.0132678e-8
Test 7(Air)>08-15Mar	HGV-4	3.5971684e-9	4.648844e-10	-4.83643e-10	-5.03077e-10	0.0669052051	-0.007764226	1.3013065e-9	-1.51014e-10	4.5779963e-8
Test 7(Air)>08-15Mar	HGV-6	3.5373201e-9	1.3459213e-9	-1.383582e-9	-1.458853e-9	0.0673495365	-0.00777824	3.8170104e-9	-4.40829e-10	1.3275562e-7
Test 7(Air)>08-15Mar	HGV-3	2.263775e-9	7.788198e-10	-8.0388e-10	-5.46874e-10	0.0677998092	-0.007712611	2.2599737e-9	-2.57085e-10	7.6906904e-8

Table 40. HGR and Uncertainty Determinations for Final Sample of Testing Involving a Second-Sample

Test	Test Temp	Spike/ Control	Reactor	1/Kelvin	HGR ft3/(hr-gal)	Std Dev HGR	Degrees of Freedom (HGR std dev)	%RSD HGR	Lower Limit (95% confidence)	Upper Limit (95% confidence)	log e (HGR)
Test 6(Air)>06Feb-05Mar	35	Control	HGV-5	0.0032451728	1.869e-9	6.29e-11	15.0	3.4%	1.735e-9	2.003e-9	-20.0979
Test 7(Air)>08-15Mar	71.5	BFS	HGV-2	0.0029014943	5.257e-8	1.57e-9	48.0	3.0%	4.941e-8	5.573e-8	-16.7611
Test 7(Air)>08-15Mar	71.5	Control	HGV-4	0.0029014943	4.863e-8	1.55e-9	48.0	3.2%	4.551e-8	5.175e-8	-16.8390
Test 7(Air)>08-15Mar	71.5	Grout-Premix	HGV-6	0.0029014943	9.906e-8	3.05e-9	51.0	3.1%	9.294e-8	1.052e-7	-16.1275

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